THE EFFECTS OF METAL ION AND LIGAND SUBSTITUTION ON THE SPECTROSCOPIC PROPERTIES OF METAL COMPLEXES

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by

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CONTENTS

SUMMARY

Metal-nitrogen stretching vibrations in Co(II), Ni(II), Cu(II) and Zn(II) chloride 4-methylaniline complexes are assigned by ^{15}N-labelling in conjunction with a consideration of the relative crystal field stabilization energies of the metal ions.

Bands in the ultraviolet electronic spectra of Cu(II) β-ketoenolate complexes are more conclusively assigned by comparison of the spectra of the β-ketoenolates, their sodium salts and the copper complexes.

The effect of ligand substitution on the infrared spectra of Cu(II) benzoylacetanilide complexes and their methanol adducts is used to assign copper-oxygen stretching frequencies. The effect of ligand substitution on the ultraviolet electronic spectra is used to estimate the extent of π-interaction in these complexes.

The infrared spectra of six ^{15}N-labelled Co(II), Ni(II), Cu(II) and Zn(II) N-salicylideneanthranilate complexes yield assignments of metal-ligand and certain ligand vibrations. These assignments are supported by observing the effects of metal ion and ligand substitution on the spectra. The shifts observed in the metal-ligand stretching frequencies are related to the relative crystal field stabilization energies of the metal ions and to the electron releasing and withdrawing capacities of the ligand substituents.

Assignments of metal-ligand vibrations in the infrared spectra of Ni(II) and Cu(II) benzoylbenzilidenehydrazone complexes and Co(II), Ni(II), Cu(II) and Zn(II) benzoylsalicylidenehydrazone complexes are made by observing the effects of metal ion and ligand substitution on the spectra.

The infrared spectra of three ^{15}N-labelled Ni(II), Co(II) and Cu(II) triarylformazan complexes yield assignments of metal-ligand and certain ligand vibrations. The effect of ligand substitution on the infrared spectra of Ni(II) triarylformazan complexes is related to the electron releasing or withdrawing capacities of the substituents.

A total of 168 complexes, of which 131 have not previously been reported, has been synthesized and discussed.

PUBLICATIONS

Parts of this work have been published as follows:

1. P.R. JOHNSON and D.A.THORNTON, *Chimia*, 28 (1974) 345. "Band Assignments in the Infrared Spectra of *p*-Toluidine and Its Complexes with Metal(II) Chlorides".

2. P.R. JOHNSON and D.A. THORNTON, *Spectros. Lett.*, 7 (1974) 293. "Infrared Spectra of Metal(II) 1,3,5-Triarylformazan Complexes".

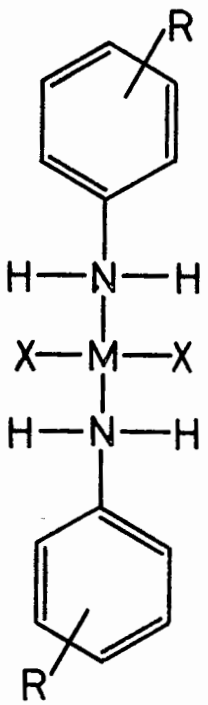
3. P.R. JOHNSON and D.A. THORNTON, *J.Inorg.Nucl.Chem.*, 37 (1975) 461. "Benzoylacetanilide Complexes of Copper(II)".

4. P.R. JOHNSON and D.A. THORNTON, *J.Mol.Structure*, (in press). "Electronic Spectra of Copper(II) β-Ketoenolates : Intraligand and Charge Transfer Transitions".

ABBREVIATIONS

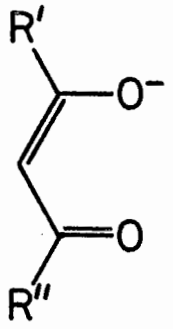
bipy	2,2'-bipyridine
CFSE	Crystal Field Stabilization Energy
CFT	Crystal Field Theory
δ	infrared bending mode
kK	kiloKayser
L	generalized ligand
LFT	Ligand Field Theory
M	generalized metal ion
MOT	Molecular Orbital Theory
ν	infrared stretching mode
phen	1,10-phenanthroline
R	generalized substituent

FORMULAE AND ABBREVIATIONS OF LIGANDS AND COMPLEXES APPEARING IN THE TEXT.



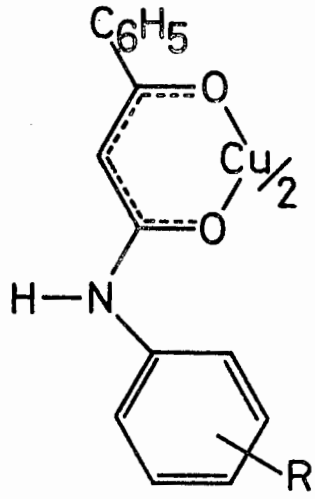
Metal(II) dihalide bis(aniline) complexes

General abbreviation: $MX_2(R\text{-}An)_2$



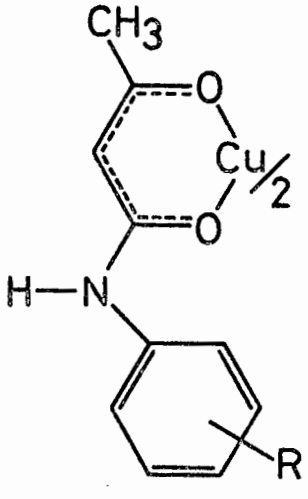
β-ketoenolates

$R' = R'' = CH_3$;	acetylacetonate	AA
$R' = CH_3$, $R'' = C_6H_5$;	benzoylacetonate	BA
$R' = R'' = C_6H_5$;	dibenzoylmethanate	DBM
$R' = CH_3$, $R'' = CF_3$;	trifluoroacetylacetonate	TFA
$R' = R' = CF_3$;	hexafluoroacetylacetonate	HFA
$R' = R'' = C(CH_3)_3$;	dipivaloylmethanate	DPM
$R' = CH_3$, $R'' = N(C_2H_5)_2$;	N,N-diethylacetoacetamide	DEAA
$R' = CH_3$, $R'' = NHC_6H_5$;	acetoacetanilide	AAA
$R' = C_6H_5$, $R'' = NHC_6H_5$;	benzoylacetanilide	BAA
$R' = CH_3$, $R'' = OC_2H_5$;	ethylacetoacetate	EAA
$R' = C_6H_5$, $R'' = OC_2H_5$;	ethylbenzoylacetate	EBA
$R' = C_6H_5$, $R'' = CF_3$;	benzoyltrifluoroacetonate	BTA
$R' = C_4H_3S$, $R'' = CF_3$;	2-thenoyltrifluoroacetonate	TTA
$R' = R'' = H$;	diformylmethanate	DFM



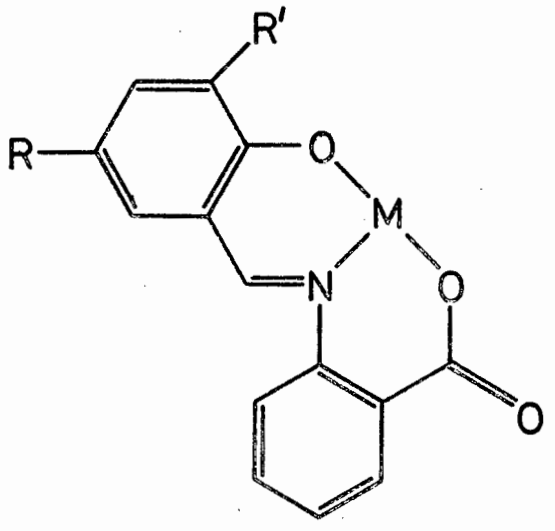
Copper(II) benzoylacetanilide complexes

General abbreviation : $Cu(BzAcR\text{-}An)_2$



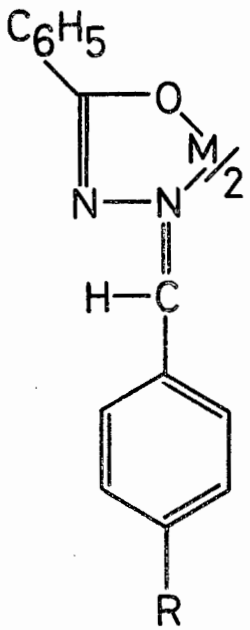
Copper(II) acetoacetanilide complexes

General abbreviation : $Cu(AcAcR\text{-}An)_2$



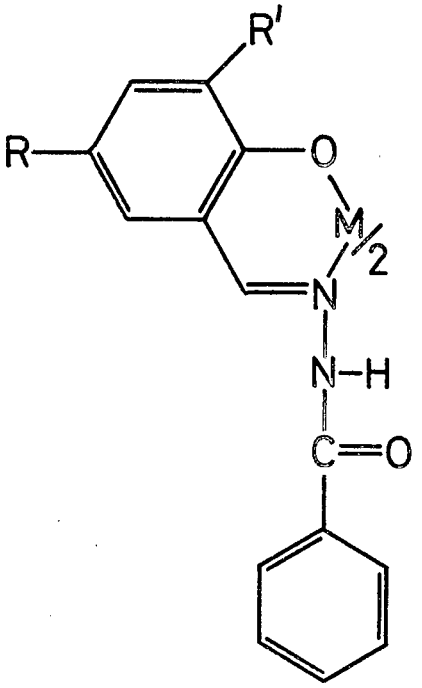
Metal(II) N-salicylideneanthranilate complexes

General abbreviation : M(R-salanth)



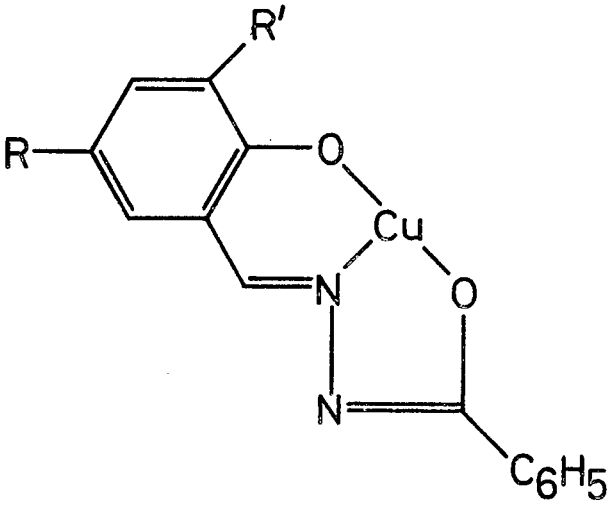
Metal(II) benzoylbenzilidenehydrazone complexes

General abbreviation : $M(BR\text{-}BH)_2$



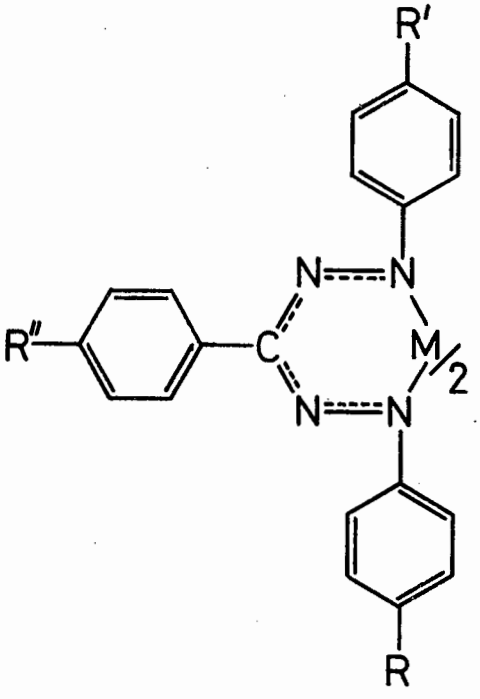
Metal(II) benzoylsalicylidenehydrazone complexes

General abbreviation : $M(BR\text{-}SH)_2$

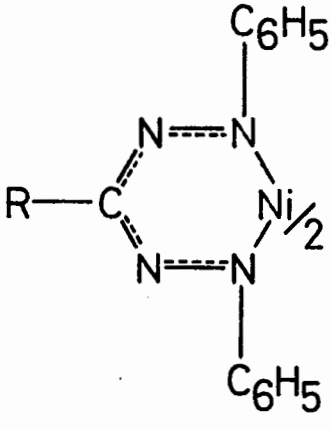


Copper(II) benzoylsalicylidenehydrazone complexes

General abbreviation : Cu(BR-SH)



Metal(II) triarylformazan complexes



Nickel(II) 3-substituted 1,5-diarylformazan complexes

I. INTRODUCTION

1. CRYSTAL FIELD ASPECTS OF INFRARED SPECTRA

Theoretical attention to the properties of transition metal complexes has resulted in the development of CRYSTAL FIELD THEORY (CFT), based on a situation in which the metal ion and the surrounding ligands are considered to interact solely by electrostatic forces. This theory was subsequently modified to take account of orbital overlap and was then termed LIGAND FIELD THEORY (LFT). The effect of the electrostatic field of the ligands is to remove the degeneracy of the d orbitals of the metal ion, the consequent changes in energy affecting some of the properties of the transition metal complexes. An alternative approach, MOLECULAR ORBITAL THEORY (MOT), in which orbitals of the transition metal complexes are formed by combination of the appropriate orbitals of the metal ion and the ligands, gives similar results to those of LFT and can also more easily take account of π-bonding.

In an octahedral ligand environment, the crystal field splits the five d orbitals into two sets of orbitals, which have an energy difference denoted by $10\,Dq$. Three of the orbitals, denoted t_{2g}, are stabilized by an amount of $4Dq$ and the other two orbitals, denoted e_g are destabilized by $6Dq$. Except for the electron configurations d^0, d^5 (high spin) and d^{10}, the splitting leads to a net lowering of the total energy of the system. This decrease in energy is termed the CRYSTAL FIELD STABILIZATION ENERGY (CFSE). The CFSE of a metal ion in an octahedral environment is given by[1]

$$\text{CFSE} = -(0.4n_{t_{2g}} - 0.6n_{e_g})10Dq$$

where $n_{t_{2g}}$ and n_{e_g} are the numbers of electrons in the t_{2g} and e_g orbitals

respectively. Jorgensen[2] has expressed $10Dq$ as

$$10Dq = fg$$

where f is a measure of the crystal field splitting power of the ligand relative to water ($f = 1$) and g is the spectroscopically determined magnitude of $10Dq$ for the octahedrally hydrated metal ion. This approach to the calculation of the CFSE has been illustrated by the case of the d orbitals in an octahedral environment. The CFSE's of metal ions in tetrahedral and square planar environments and when splitting of f orbitals occurs can also be calculated.

The CFSE has been shown[1,3] to account for the variation of bond distances, lattice energies, heats of ligation and other thermodynamic properties through an isostructural series of isovalent metal compounds of constant ligand composition. The CFSE represents only a small part of the energy changes accompanying the metal-ligand interaction and therefore only becomes significant when other factors influencing the properties are constant or vary smoothly in a predictable manner through the set of compounds being studied. Since the CFSE influences the M-L bond strength, the M-L force constants of an isostructural series of complexes of different metal ions would be expected to show a similar variation with d orbital population to that exhibited[3] by thermodynamic properties. This same variation should then, in the absence of any significant mass effect, hold for the M-L stretching frequencies, νM-L, in the infrared spectra of these complexes.

This was shown to be the case by Sacconi and Sabatini[4,5] for metal (II) hydrazine complexes and by Thornton and coworkers[6-14] in several series of complexes of the first transition metal series

and has been extended to a few series of complexes of the second transition metal series and the lanthanide series. The νM-O values of many β-ketoenolate complexes of metal(III) ions show a correlation with the relative values of the CFSE's of these ions[6]. Similar results have been obtained for the variation of νM-L of metal (II) 2,2'-bipyridyl and 1,10-phenanthroline complexes[7], the metal (II) acetylacetonates[8] and their base adducts[8], the potassium salts of the metal (II) tris(acetylacetonates)[8], the metal (II) and metal (III) tropolonates[9] and 2-thenoyltrifluoroacetonates[10], metal (III) oxalate and cyanide complexes[11], the metal (II) anthranilates[12], the lanthanide (III) tropolonates[13] and the lithium salts of the lanthanide (III) tetrakis (tropolonates)[14]. The correlation of νM-L with CFSE has been used[15,16,17] for assignment of this vibration in a number of metal (II) salicylaldimine complexes.

In order to isolate the crystal field contribution to the M-L stretching frequency it is necessary to have a standard of comparison from which the crystal field effects are absent. This is provided by the d^0, d^5 (high spin) and d^{10} configurations for the transition metals and the f^0, f^7 and f^{14} configurations for the lanthanides. The contribution of the CFSE to νM-L is taken as the difference between the observed frequency, ν, and the frequency, ν_0, given by the appropriate point on the interpolation line through the points for the d^0, d^5 and d^{10} or f^0, f^7 and f^{14} configurations. The value of $\nu-\nu_0$ is considered to be the crystal field contribution to the total frequency and has been shown to yield a good correlation with calculated values of the CFSE[6-14].

2. SUBSTITUENT CONSTANTS.

Quantitative relationships between the electronic effects of substituents in organic compounds and their physical and chemical properties have been widely studied[18]. One of the earliest and also the most familiar of the relationships is the Hammett equation[19], which relates equilibrium constants and rate constants for reactions of benzene derivatives substituted in the 3- and 4- positions with the nature of the substituent. The Hammett equation may be written

$$\log \frac{k}{k_0} = \rho\sigma$$

where k and k_0 are the equilibrium or rate constants for reactions involving substituted and unsubstituted compounds respectively, σ is the substituent constant and ρ is the reaction constant.

Hammett originally studied the ionization constants of substituted benzoic acids. For this series of reactions, he set ρ equal to unity and determined two sets of substituent constants σ_m and σ_p for 3- and 4-position substituents, respectively. Investigation of other series of reactions showed the general validity of the equation once the values of ρ for the various series had been determined.

The Hammett relationship makes it possible to calculate the equilibrium or rate constant for a reaction of a substituted benzene derivative from its σ value and the corresponding constant of the unsubstituted compound, when the value of ρ for that reaction is known.

The reaction constant ρ is a measure of the sensitivity of the reaction to ring substitution. The substituent constant σ depends solely on the nature and position of the substituent and is a measure of the electron withdrawing or electron releasing ability of the substituent, relative to the hydrogen atom, which has σ set equal to zero.

A positive value of σ indicates that the substituent withdraws electrons relative to the hydrogen atom, a negative value indicates that electrons are released. Withdrawal or release of electrons takes place by a combination of the inductive (or field) and mesomeric (or resonance) effects of the substituent, the σ value indicating the resultant effect of both phenomena.

Jaffe reviewed[20] the values of Hammett's substituent constants, recalculating σ from more recent values of equilibrium and rate constants, obtained for a wide series of reactions. McDaniel and Brown[21] redetermined σ_m and σ_p values for the ionization of substituted benzoic acids and recommended that these values be used for the substituent constants rather than the mean values derived from all available reactions. Their values will be used in this work as being the most precisely determined set available.

The separation of the σ values into their inductive (or field) effect and resonance (or mesomeric) effect followed the work of Taft[22,23] and Roberts and Moreland[24] who extended the approach of Hammett in order to evaluate inductive effects in aliphatic, as opposed to aromatic, systems. Taft defined a substituent constant σ* based on the rates of hydrolysis of aliphatic ethyl esters and Roberts and Moreland put forward a similar substituent constant σ' derived from reactivities in the 4-substituted bicyclo-[2.2.2]-octane-1-carboxylic acid system. Taft[25] then defined $\sigma_I = 0.45\ \sigma^*$ (to take into account the fact that in his aliphatic series the reference compound was ethyl acetate, with a CH_3 substituent, and not ethyl formate, with H as substituent) and proposed that σ_I (or σ') represents a measure of the inductive contribution to the σ values in aromatic systems. The resonance contribution σ_R to the σ_p and σ_m values

was taken as $\sigma_p - \sigma_I$ or $\sigma_m - \sigma_I$ for the 4- or 3-position substituents, respectively. Dewar and Grisdale[26] calculated field (F) and mesomeric (M) constants for each substituent from the values of σ_p and σ_m with the intention of obtaining substituent constants applicable to other ring systems. This approach was extended by Swain and Lupton[27] who defined pure Field (F) and resonance (R) constants for each substituent and showed that all the different σ series, such as σ_I, σ_R, σ', σ^* and numerous others which have been proposed by various workers may be calculated from the equation $\sigma = fF + rR$ where f and r are the appropriate weighting factors.

The relationship between substituent constants and the frequencies of various vibrations in the infrared spectra of aromatic, heterocyclic and aliphatic compounds and metal complexes has been studied by a considerable number of workers. It has been shown that the symmetric and asymmetric νN-H of anilines[28] and amines[29], νO-H of phenols[30] and νC=O of aliphatic ketones[31] vary linearly with σ or σ^*. Correlations have been established between substituent constants and νC=O and νM-O in alkylamine, aniline and pyridine adducts of Ni (II) and Zn (II) acetylacetonates[32,33], νU=O in alkylamine adducts of uranyl dibenzoylmethanate[34] and pyridine adducts of uranyl acetylacetonate[35], νM-L in metal (II) salicylaldimine complexes[15,16,17], νM-L in metal(II) anthranilates[12] and 8-hydroxyquinolates[36], and νCo-N for aniline and pyridine adducts of the dinitrobis (acetylacetonato) Co (III) ion[37,38].

3. METHODS OF ASSIGNING THE METAL-LIGAND VIBRATIONS IN THE INFRARED SPECTRA OF METAL COMPLEXES.

The assignment of metal-ligand vibrations in metal complexes is of great importance since knowledge of their frequencies gives direct information about the nature of the metal-ligand bond and the structure of the compound. Assignments are often rendered difficult because the interpretation of the infrared spectra is complicated by vibrational coupling, the appearance of vibrations activated by complex formation, intermolecular interactions, lattice modes and lowering of symmetry[39].

Metal-ligand vibrations have been assigned by the following methods:

1. Theoretical calculations such as normal coordinate analysis using known bond lengths and force constants lead to values for M-L and other vibrations. Vibrations in complexes of acetylacetone[40-44] and bipyridine[45] have been assigned by this method.

2. Comparison of the infrared spectrum of the complex with that of the ligand leads to identification of bands which appear only in the spectrum of the complex as probable M-L vibrations. This method has the disadvantage that some ligand vibrations are activated by coordination[46].

3. For complexes of a particular metal with a range of very similar ligands the M-L vibrations would be expected to appear in the same region of the spectrum. This method has been used to assign νCu-N in the compounds CuX_2L_2 (X = Halogen, L = substituted pyridine)[47], νNi-O in substituted pyridine adducts of Ni (II) acetylacetone[33] and νM-O in metal β-ketoenolates[48].

4. For isostructural complexes of identical ligands with different metals or differing oxidation states of a metal the M-L vibrations would be expected to follow the order of the CFSE's of the metal ions[6-14].

5. The replacement of an atom by an isotope will result in a change of the frequency of any vibrations involving that atom. If the isotopically substituted atom is the metal or the ligand donor atom, then the M-L vibrations can be identified.

Since the absorption of electromagnetic radiation in the infrared region by molecules is dependent on the masses of their constituent atoms, a labelled molecule will usually show an infrared spectrum which is different from that of the normal molecule. The spectral differences observed depend on the ratio of the masses of labelled and normal atoms, the larger the ratio the greater the isotopic shift. The largest isotopically-induced shifts (up to about 1300 and 1000 cm^{-1}, respectively) are observed for tritiated and deuterated molecules[49]. Isotopic shifts for substitutions involving atoms other than hydrogen are considerably less, but shifts of up to 40 cm^{-1} have been observed in the spectra of ^{18}O-labelled molecules[49]. The size of the isotopic shift of an infrared band also depends on other factors such as hydrogen bonding in the molecule (which can reduce the expected shift) and the extent of vibrational coupling of bands. The more a part of the molecule containing the labelled atom contributes to a coupled vibration, the larger will be the isotopic shift.

The expected isotopic shifts can be calculated[49] by assuming the atom in question to be part of a simple harmonic oscillator.

The vibrational frequency of a diatomic molecule can be represented by the equation

$$\nu = \frac{1}{2\pi c}\left[\frac{k}{\mu}\right]^{\frac{1}{2}}$$

where ν = vibrational frequency expressed as a wavenumber

k = harmonic force constant

μ = reduced molecular mass

c = velocity of electromagnetic radiation.

Hence, the isotopic shifts may be calculated from

$$\nu_i/\nu = (\mu/\mu_i)^{\frac{1}{2}}$$

where the subscript i refers to the labelled molecule. This is a good approximation provided the vibration of the two atoms concerned is not substantially affected by the rest of the molecule.

The isotopes which have been most commonly employed in assigning νM-L in metal complexes are ^{15}N and ^{18}O. The only nitrogen isotope which can practicably be used for labelling purposes is the stable isotope of mass 15, with a natural abundance of 0.38%, since the half lives of the other isotopes are all less than eleven minutes. The largest shifts are observed for various ^{15}N-H, C=^{15}N, ^{15}N=O and C≡^{15}N stretching vibrations but significant shifts are also found for ^{15}N-H bending and ^{15}N=N, C-^{15}N and M-^{15}N stretching vibrations. The most readily available oxygen atom for labelling purposes is the stable isotope of mass 18, with a natural abundance of 0.20%. Most of the shifts reported are for various X=^{18}O and X≡^{18}O stretching vibrations where X is C, N, P, As, S, V or U, but significant shifts have also been observed of ^{15}O-H, C-^{18}O and M-^{18}O stretching vibrations.

Labelling of the ligand donor atom has been used, for example,

to assign νM-L in salicylaldimine complexes [15,16,50], acetylacetonate complexes [51,52,53], anthranilate complexes[12], tropolonate complexes[54] and nitrosyl complexes[55,56]. Labelling of the metal atom has been used in α-diimine complexes[57], acetylacetonate complexes[58], phosphine complexes[59,60,61], alkene complexes[62], diamine complexes[63,64], carboxylate amine complexes[65] and tropolonate complexes[66].

The advantages of labelling the ligand donor atom as opposed to the metal atom are, firstly, that the isotopically-induced shifts are generally larger owing to a more favourable μ/μ_i ratio and, secondly, that the available ligands can often be obtained in larger quantities than the oxides of the metal isotopes with a consequent reduction in the difficulties of complex preparation and measurement. A disadvantage of labelling the ligand atom is that some bands originating in ligand vibrations involving the donor atom may be incorrectly assigned to νM-L. Labelling the metal atom has an obvious advantage in those cases where synthesis of the ligand containing the required isotope is difficult, but the availability of two isotopes of a metal atom may be limited.

4. METAL HALIDE AMINE COMPLEXES

Complexes of aromatic amines with metal(II) halides have been widely reported but the assignments in the infrared spectra of vibrations involving the nitrogen atom of the amine and in particular the M-N stretching vibrations have not been determined with any certainty.

A number of workers have reported the preparation of complexes of aromatic amines with metal halides but the spectroscopic and structural properties have not been investigated until comparatively recently. Infrared spectra[67-82,94], electronic spectra[68,69], magnetic moments[68,69,83-86], crystal structures[87-90], stability constants[91] and thermodynamic properties[92] have been reported.

X-ray crystallographic studies of $CoCl_2(4\text{-}CH_3an)_2$[87,89] $CoI_2(4\text{-}CH_3an)_2$[90] and $ZnCl_2(4\text{-}CH_3an)_2$[88] have shown a tetrahedral distribution of ligands around the metal ion. Electronic spectra of Ni complexes[68,69] are consistent with an octahedral arrangement of ligands around the metal ion. Investigations of the magnetic properties have shown three unpaired electrons for Ni complexes[84,85] and four unpaired electrons for Co complexes[83,86]. These values are not diagnostic of stereochemistry but do not conflict with a polymeric octahedral and a tetrahedral structure, respectively, suggested by other data. No X-ray crystallographic study of a Cu(II) halide aniline complex has been reported but in $CuCl_2(pyridine)_2$[93] there is a square planar arrangement of ligands around the copper ion with longer Cu-Cl bonds perpendicular to the coordination plane, thus forming chains of molecules.

Empirical assignments of bands in the infrared spectra have

been proposed by a number of workers. Jungbauer and Curran[67] suggested that a band between 370 and 450 cm^{-1} is associated with nitrogen to metal stretching vibrations. Ahuja and coworkers[68,69] considered that bands between 350 and 425 cm^{-1} are most likely derived from metal-nitrogen vibrations. They pointed out that the frequency of vibration is dependent upon the coordination arrangement about the metal, occurring at higher values for the tetrahedral Co and Zn and tetragonal Cu complexes than for the octahedral Mn and Ni complexes.

A number of Russian workers have investigated the infrared spectra of metal halide aniline complexes. It was concluded that there is an inverse relationship between the frequency of νN-H and νM-N, the N-H bond becoming weaker with increase of the M-N bond strength[76,77,79,81]. The frequencies of νM-N, which was assigned to a band in the region 345-385 cm^{-1} were found to be metal-sensitive in the order Co>Ni>Cu<Zn for the $MCl_2(an)_2$ complexes[76]. Bands between 140 and 330 cm^{-1} were assigned to νM-Cl in $MCl_2(an)_2$ complexes[72,75]. Substitution on the aniline ring by $-CH_3$ and $-OCH_3$ groups in the 4-position gave a higher frequency for νM-N than the unsubstituted complex[79,94].

In aniline, bands have been assigned by isotopic labelling techniques. A number of workers have studied N-deuterated aniline[95-98] and a study of ^{15}N-substituted aniline was carried out by Tsuboi[99]. Besides the obvious N-H stretching and bending vibrations, they assigned a band at about 1270 cm^{-1} to the C-N stretching vibration. Their assignments of other bands were not in complete agreement but bands at about 1120 cm^{-1} and 700 cm^{-1} were assigned to vibrations involving the NH_2 group.

5. ELECTRONIC SPECTRA OF COPPER(II) β-KETOENOLATE COMPLEXES.

The ultraviolet electronic spectra of transition metal β-ketoenolate complexes have been widely studied[100]. Hückel semi-empirical calculations leading to the placement of energy levels have been carried out[101-106] and have led to general agreement on the assignments of the transitions. However, there has been disagreement on the assignment of a band occurring near 40 kK (1kK = $10^3 cm^{-1}$) in the Cu(II) complexes.

In Cu(II) β-ketoenolate complexes, two bands are found in the region between 28 and 45 kK. The lower energy band, occurring in the range 28 to 37 kK, has been unanimously assigned, by virtue of its similarity in energy to a transition in β-ketoenolate ligands and anions and by theoretical calculations[101-106] to the $\pi_3 \rightarrow \pi_4^*$ transition. The higher energy band, occurring in the range 36 to 45 kK, was originally suggested[101] to be one component of the $\pi_3 \rightarrow \pi_4^*$ transition moved to higher energy by π-bonding. It was subsequently reassigned, mainly on the grounds of theoretical calculations[104,105] supported by its sensitivity to α-substitution[103] and lack of sensitivity to γ-substitution[107], to a charge transfer transition from an oxygen σ-bonding or nonbonding orbital to the copper $3d_{xy}$ orbital.

Although this revised assignment has not been questioned, in some recent work[108] the earlier assignment of this band to a $\pi \rightarrow \pi^*$ transition was nevertheless adopted. Furthermore, there is no record in the literature of an explicit assignment of this band in a copper β-ketoenolate complex where an aryl or heterocyclic ring is conjugated with the chelate ring.

6. METAL CHELATES OF ACETOACETAMIDES, ACETOACETANILIDES AND BENZOYLACETANILIDES.

The acetoacetamides, acetoacetanilides and benzoylacetanilides, having the general formula RC(OH)CHC(O)NR'R", are a novel class of β-ketoenolates having an NR'R" group bound to the β-carbon atom. R' and R" are both alkyl groups in the acetoacetamides, whereas in the acetoacetanilides and benzoylacetanilides R' is a hydrogen atom and R" is an aryl group. The metal complexes of these β-ketoenolates, and particularly those of benzoylacetanilide have not been widely studied.

These ligands allow the possibility of coordination through two oxygen atoms or through an oxygen atom and the nitrogen atom. In both cases one proton would be lost on coordination and a six-membered chelate ring formed. It was at one time suggested[109] that coordination occurs through nitrogen and oxygen atoms but subsequent spectroscopic evidence[110] and the linear relationship between the dissociation constants of the ligands and the stability constants of the complexes in a series of copper acetoacetanilide complexes[111] has led to the conclusion that coordination occurs through the two oxygen atoms.

The first preparation of a complex of this class of ligands, namely Cu(II) acetoacetanilide, was reported[112] in 1886. A number of substituted Cu acetoacetanilide complexes was reported[113] in 1939, but it was not until after 1960 that the properties of the complexes were studied to any great extent.

Most work has been carried out on the complexes of acetoacetamides and acetoacetanilides. Stability constants[111,114-125], thermodynamic values[108,117,124], magnetic moments[108,126-133] and

electronic[108,109,120,122,128-131,133-140], infrared[108,131-133,137,138,141-146], electron spin reconance[147], mass[148-150] and Mössbauer[151] spectra have been determined. A number of analytical applications, including gravimetric[145,152] and spectrophotometric [122,153,154] determinations have been described. The formation of pyridine adducts [128,135] and mixed chelates with α-diimines[134,135] have been reported. Complexes of Na(I), Hg_2(II), Be(II), Co(II), Ni(II), Cu(II), Zn(II), Hg(II), Al(III), Cr(III), Fe(III), Y(III), Pr(III),Nd(III), Sm(III), VO(IV) and UO_2(VI) have been reported.

The complexes of benzoylacetanilides have received less attention than those of acetoacetamides and acetoacetanilides. Only three reports[111,155,156] exist on the Cu(II) complexes of benzoylacetanilides, a study of which comprises one section of this thesis. Properties of benzoylacetanilide complexes of Na(I)[139,140], Cr(III)[133,157], Fe(III)[158-162], Nb(V)[163], Ta(V)[163], VO(IV)[164], Ti(IV)[159,165], TiO(IV)[166], UO_2(VI)[167,168] and MoO_2(VI)[169] have also been reported. Stability constants[111,160-162], thermodynamic values[160-162], magnetic moments[133,155,157,158,164,165,167,169] and electronic[133,139,155-158,163,164,167,169], and infrared[133,155-158,163-165,167] spectra have been determined. Gravimetric[159,166,170,171] and spectrophotometric[159,161,162,166,168] determinations of metal ions using benzoylacetanilides as reagents have been described. The formation of methanol adducts of UO_2(VI) benzoylacetanilides has been reported[167].

Wolf and Wetzel[111] reported the stability constant of CuL_2 (HL = benzoylacetanilide). Syamal[155] reported the electronic and infrared spectra and the magnetic moment of the copper complex. The magnetic moment was found to be 1.40 Bohr magnetons which was considered

to be indicative of the presence of a Cu-Cu bond. The infrared spectrum showed two bands at 1580 and 1600 cm^{-1}, considered to be due to νC=O, the frequencies in the ligand spectrum between 1670 and 1700 cm^{-1} being lowered on coordination. A band at 475 cm^{-1} was empirically assigned to νCu-O. In the electronic spectrum, an intense band at 31.3kK assigned to a transition in the ligand, bands at 22.7kK and 27.0kK attributed to the Cu-Cu bond and a band in the region of 16kK assigned to the $d \rightarrow d$ transitions, were observed. It was considered that the spectrum was consistent with Cu-Cu bonding and that the frequency of the 16kK band indicated considerable distortion from square planar stereochemistry.

Syamal has also reported electronic and infrared spectra of Fe(III)[158], Cr(III)[157] and UO_2(VI)[167] benzoylacetanilide complexes. It was concluded that benzoylacetanilide is very close to acetylacetone in the spectrochemical series.

7. METAL COMPLEXES OF N-SALICYLIDENEANTHRANILIC ACIDS.

N-Salicylideneanthranilic acid is a novel dibasic salicylaldimine Schiff base ligand with four potential donor atoms. Metal complexes of Schiff bases were first isolated by Ettling[172] in 1840 and were characterized by Schiff[173] in 1869. Schiff bases contain the azomethine group (-RC = N-) and are usually formed by condensation of an amine with an active carbonyl compound. Of all the Schiff base complexes, those derived from salicylaldehyde, where the -OH group is so placed that a six-membered chelate ring can be formed with a metal ion, have been the most widely studied. The advantage of these salicylaldimine ligands is that they allow the preparation of a wide variety of complexes whose properties are often dependent on the detailed ligand structure and on the metal ion coordinated.

Several reviews[174-178] have been published concerning the chemistry of salicylaldimine complexes in general but none has been published on the complexes of N-salicylideneanthranilic acids. The first reported preparation of complexes of N-salicylideneanthranilic acid was by Ray and Mukkerjee[179] who isolated compounds of copper and cobalt with one doubly deprotonated ligand molecule per metal ion and an anionic complex of nickel with two doubly deprotonated ligand molecules and one anthranilate ion per nickel ion. Subsequent work[180-193] confirmed a general stoichiometry for the complexes of divalent ions of ML (H_2L = N-salicylideneanthranilic acid), one or more water or other base molecules per metal ion often being present. Complexes of Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), VO(IV) and UO_2(VI) have been reported and characterized. The 2,2'-bipyridine and 1,10-phenanthroline adducts of the complexes of Cu(II) and VO(IV) have

also been reported[194-197]. Complexes of the very similar ligand N-2-hydroxy-1-naphthylideneanthranilic acid have been reported[198] with Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Pd(II) and UO_2(VI). Magnetic moments[179-184,186,187,191-198], electronic[186,187,194-197] and infrared spectra [186,187,193] and stability constants[199] have been reported. Only the Cu(II) and Ni(II) complexes have been investigated in any detail. The infrared spectral investigations have been solely concerned with the assignment of the νC=O vibration and infrared spectra have not been reported below 1500 cm^{-1}. Electronic spectroscopic and magnetic evidence[186] indicates that the Ni complexes have octahedral symmetry of donor atoms, although the picture is somewhat confused. The magnetic moments[179,181-184] in the case of the copper complexes show a normal value corresponding to one unpaired electron. Since the magnetic moments of the analogous N-salicylidene-2-aminophenol complexes are subnormal, indicating Cu-Cu interaction through bridging oxygen atoms[200], a dimeric structure containing an eight-membered ring with two copper atoms, sufficiently far apart to prevent any interaction, was proposed[184]for the copper complexes.

8. METAL COMPLEXES OF AROYLARYLIDENEHYDRAZONES.

The study of metal complexes of aroylhydrazides and hydrazones has become of interest because the antituberculotic activity of hydrazide drugs such as isonicotinic hydrazide has been attributed[201-203] to their ability to form complexes with Cu(II) ions. It is also of interest that the hydrazide residue may react with metal ions in the ketonic form ($-C(O)-NH-NH_2$), without loss of a proton,or in the enolic form ($-C(OH)=N-NH_2$) with loss of the enolic proton[204]. In both cases a five-membered chelate ring is formed, coordination taking place through the oxygen atom and the terminal nitrogen atom.

Reaction of hydrazides with compounds containing an oxo group results in the formation of a class of Schiff bases, generally called aroylarylidenehydrazones ($RC(O)NHN=CR'R''$). In particular, reaction of benzoic acid hydrazide with benzaldehyde and salicylaldehyde give benzoylbenzilidenehydrazone and benzoylsalicylidenehydrazone, respectively. The physical properties of metal complexes of these ligands have not been widely studied.

Benzoylbenzilidenehydrazone (BBH) is a bidentate ligand which reacts with metal(II) ions in the ketonic or enolic form. El Sayed and Iskander[205] investigated the reactions with metal salts. With nickel chloride, paramagnetic complexes having an electronic spectrum typical of octahedral symmetry were isolated. The infrared spectrum shown a band at 3200 cm^{-1}, assigned to $\nu N-H$. It was concluded that the ligand reacts in the ketonic form, complexes of the formula $Ni(HL)_2Cl_2$ (HL = BBH) being formed. With nickel acetate, diamagnetic, orange complexes showing no band in the infrared spectrum in the region 3000 - 4000 cm^{-1} are

isolated. In these and the analogous copper complexes, the ligand is considered to react in the enolic form, losing a proton and forming complexes of formula ML_2. Complexes of benzoylalkylidenehydrazone[206], benzoylisopropylidenehydrazone[207], benzoylfurfurilidenehydrazone[208] and benzoylcinnamilidenehydrazone[208] have also been reported.

Benzoylsalicylidenehydrazone (BSH) and the analogous acyl compounds are potentially tridentate ligands, whilst salicoyl-salicylidenehydrazone is a potentially tetradentate ligand. However, all the donor atoms of one ligand molecule are not always used in co-ordination to a particular metal ion. Sacconi first reported[209,210] complexes of ligands of this type in an investigation of the action of hydrazides on nickel salicylaldehyde complexes. The complexes formed have the formula $Ni(HL)_2$ (H_2L = aroyl- or acyl-salicylidenehydrazone). The complexes are greenish-yellow in colour and have magnetic moments in the range 3.0 to 3.4 Bohr magnetons. It was suggested that they have a tetrahedral configuration. It was assumed that coordination occurs through the Schiff base oxygen and nitrogen atoms and the hydrazide residue is not coordinated to the nickel ion. It was assumed to exist in the enolic form (C_6H_5-C(OH)=N-) on the grounds that the complexes are soluble in sodium hydroxide solution and are reprecipitated by carbon dioxide or acetic acid. Complexes were also prepared[209,211] having the formula NiL.B (H_2L = aroylsalicylidenehydrazone, B = benzoic acid hydrazide, ammonia or other base). These are orange and diamagnetic and were assumed to have a square planar configuration.

Ohta[212,213] prepared complexes CuL, CuL.B and NiL.B (H_2L = aroyl- or acylsalicylidenehydrazone, B = water, ammonia or pyridine).

Two of the acyl- Cu(II) complexes were shown by cryoscopic measurement to have a molecular mass twice that of the empirical formula CuL. Infrared spectra were reported in the range 1700 to 5000 cm^{-1}.

The magnetic moments of four benzoylsalicylidenehydrazone complexes of Cu(II) with empirical formulae CuL were reported[184] in the range 1.02 to 1.20 Bohr magnetons. The monopyridine adducts have values in the range 1.82 to 1.84. Magnetic moments for Cu(II) compounds with values below that expected for one unpaired electron have been extensively reported and the phenomenon has been the subject of a review[200]. Such behaviour is a consequence of the formation of dimeric molecules, two different structures being found. The one structure, typically represented by Cu(II) acetate, contains a Cu-Cu bond, and the other contains two Cu atoms bridged by two oxygen atoms. This second type, found with tridentate ligands and pyridine N-oxides, occurs with the benzoylsalicylidenehydrazone complexes of Cu. Reaction with base destroys the dimeric structure and the base molecule occupies the fourth coordination position, a normal magnetic moment resulting.

Narang and Aggarwal[214] prepared complexes of salicyloylsalicylidenehydrazone, which is a potentially tetradentate ligand, with Mn(II), Fe(II), VO(IV), TiO(IV), Co(II),Ni(II) and Cu(II). A number of different structures were postulated to account for the experimental results. Different products were obtained depending on the conditions under which reaction takes place. The complexes with Co, Ni and Cu are of relevance to the complexes discussed in this thesis. Refluxing the ligand with metal chloride in ethanol gives complexes $Co(H_2L)_2$, $Cu(H_2L)_2$ and $Ni(HL)(H_2O)$ (H_3L = salicyloylsalicylidenehydrazone). Mixing an

alkaline solution with an aqueous solution of metal salt followed by neutralization with acetic acid gives complexes $Co(H_2L)_2$, $Ni(HL)(H_2O)_2$ and Cu(HL). A $Co(HL)(H_2O)_2$ complex is also reported, its method of preparation not being given. The M(HL) complexes are considered to be dimeric with bridging salicylidene oxygen atoms, but the copper complex has a magnetic moment of 1.6 Bohr magnetons which is not a decidedly low value, which would be expected for a dimeric structure. In the $M(H_2L)_2$ complexes the ligands are considered coordinated as in the benzoylsalicylidenehydrazone complexes described above, but with the hydrazide residue in the keto form and the salicyloyl hydrogen atom hydrogen bonded to this oxygen atom. A number of bands in the infrared spectra were empirically assigned. These are:
$\nu C=O$ and $\nu C=N$ between 1600 and 1620 cm^{-1}, Amide II (indicated to be $\nu C-O(\phi)$) near 1560 cm^{-1}, Amide III ($\nu C-N$) near 1380 cm^{-1}, $\nu C-O$ near 1250 cm^{-1}, $\nu N-N$ near 1040 cm^{-1}, $\nu M-O$(phenol) near 580 cm^{-1}, $\nu M-O$(carbonyl) near 490 cm^{-1} and $\nu M-N$ near 330 cm^{-1}. It was stated that $\nu M-O$(phenol) would be expected at a higher frequency than $\nu M-O$(carbonyl).

Dutta and Sen Gupta reported[215] infrared and electronic spectra and magnetic moments of 2,2'-bipyridyl and 1,10-phenanthroline adducts of benzoylsalicylidenehydrazone and salicyloylsalicylidenehydrazone complexes of VO(IV). They concluded that the complexes had an octahedral geometry.

With the exception of the work of Narang and Aggarwal[214] the infrared spectra of aroylarylidenehydrazone complexes have not been previously reported in the region below 650 cm^{-1}. Co and Zn complexes of benzoylsalicylidenehydrazone have not been previously reported.

9. METAL CHELATES OF FORMAZANS.

The formazan structure is a ligand system of wide chelating potential. Formazans and their metal complexes have been widely investigated with respect to their suitability as dyestuffs and it is to this field that most of the published work pertains[216]. Formazans have also been proposed as analytical reagents for a wide variety of metal ions[216].

Formazans were first prepared in 1892 by von Pechman[217] and Bamburger and Wheelwright[218] but were not intensively studied before about 1940. The first preparation of metal complexes of formazans was reported by Hunter and Roberts[219] in 1941. They prepared Co(II), Ni(II) and Cu(II) complexes of a number of substituted triphenylformazans. Subsequent studies have been almost exclusively on Co, Ni and Cu complexes with a few reports of Cr(III) and UO_2(VI) complexes. Ligands of a variety of types, including substituted aryl or heterocyclic groups on the terminal nitrogen atom and substituted aryl or other groups on the carbon atom, have been used for complex formation. Infrared spectra[220-224], electronic spectra[225-229], magnetic moments[228,230,231], stability constants[232,233], Raman spectra[223] and a crystal structure[234] have been determined. A section on metal complexes of formazans is included in two published reviews[178,216].

The first detailed study of the infrared spectra of triarylformazans and their metal complexes was reported by le Fevre, Sousa and Werner[220] who were mainly concerned with the assignment of νN=N in the ligands and their copper complexes. They empirically assigned bands at about 1450 cm^{-1} in the ligands and 1250 cm^{-1} in the complexes to this vibration and bands at about 1330 cm^{-1}, 1230 cm^{-1} and 1150 cm^{-1} in both

the ligands and the complexes to C-N vibrations without specifying the bond order or the specific atoms involved in the vibration. A later study of the infrared spectra of a number of substituted triarylformazans and their nickel complexes was carried out by Arnold And Schiele[221]. In the ligands, they assigned bands near 1510 cm^{-1} to νC=N, between 1290 and 1315 cm^{-1} to the exocyclic νC-N and near 1230 cm^{-1} to νC-N within the formazan skeleton. In the Ni complexes, they empirically assigned bands near 1280 cm^{-1} to νC=N, near 1260 cm^{-1} to νN=N and between 1290 and 1300 cm^{-1} to the exocyclic νC-N. These two investigations represent the only detailed work on the infrared spectra of metal formazan complexes. The spectra of Ni and Cu triarylformazan complexes have not been reported below 650 cm^{-1} whilst those of Co triarylformazan complexes and metal complexes of other formazan ligands have not been reported at all.

Otting and Neugebauer[235] investigated the infrared spectra of triphenylformazan and N,N'-diphenylformazans where the group attached to the carbon atom was either $-COOCH_3$ or $-COOC_2H_5$. They isotopically labelled one or both of the nitrogen atoms bonded to the carbon atom and by this means assigned bands near 1510 cm^{-1} to νC=N, near 1350 cm^{-1} to νN=N, between 1230 and 1320 cm^{-1} to νC-N and between 1000 and 1050 cm^{-1} to νN-N. Other bands between 400 and 1000 cm^{-1} showing ^{15}N-sensitivity were not assigned.

Irving, Gill and Cross[228] determined the electronic spectra and magnetic moments of Ni complexes of 3-methyl-1,5-diphenylformazan. The spectra show prominent bands at about 360, 420 and 780 nm in benzene solution. They tentatively assigned the band at 420 nm (23.8kK) to a $3d \rightarrow 4s$ transition and stated that its presence indicated a dsp^2 electronic configuration. From this information and the diamagnetic

character of the complexes they concluded the structure of the complexes is essentially square planar with either buckling of the chelate rings or distortion towards a tetrahedral structure. They were not able to prepare the Co and Zn complexes or solid pyridine adducts of the Ni complexes.

Ermakova, Krylov and Postovskii[231] determined the magnetic moments of a number of Co, Ni and Cu complexes of variously substituted triarylformazans. They found that the Co and Cu complexes have one unpaired electron and that the Ni complexes are diamagnetic. They concluded that both the Co and Ni complexes have square planar structures.

Dale[234] showed by X-ray crystallography that in bis(1-phenyl,3-methyl,5-p-tolylformazanato) nickel(II) there is a square planar arrangement of donor atoms around the Ni atom and the chelate rings are buckled along the lines joining the donor atoms. The aryl rings lie above and below the chelate rings, which are parallel. A stepped formation, similar to that found in a number of bis(N-arylsalicylaldimine)Ni(II) complexes[236], therefore exists in this complex.

Price[230] investigated the conditions of formation of Cu and Co complexes of a number of bi-, tri- and tetra-dentate formazans. In particular he found that the complex formed by the reaction of 1,3,5-triphenylformazan with Cu(II) acetate in hot ethanol (the method of preparation used by Hunter and Robert[219]) has a magnetic moment of 1.4 Bohr magnetons, whereas the complex formed if the ligand is extracted from a thimble into a methanol solution of Cu(II) acetate, is diamagnetic. He considered the latter to be a complex of Cu(I), coordinated by a ligand molecule and a deprotonated ligand molecule, thus having the formula Cu(I)L.HL (HL = 1,3,5-triphenylformazan) and that in the former case a mixture of $Cu(II)L_2$ and Cu(I)L.HL is produced. He obtained

an identical diamagnetic complex by extraction of the ligand into a methanol solution of Cu(I) chloride and potassium acetate.

This reductive behaviour of formazans towards Cu(II) ions is well known and is used as a method of producing tetrazolium cations from formazans. Hirsch[226] reported the formation of a Cu(I) complex of 3-acetyl-1,5-diphenylformazan, having, in this case, one deprotonated ligand molecule coordinated to the Cu(I) ions.

II. EXPERIMENTAL

1. PHYSICAL METHODS.

(i) Infrared spectra.

Infrared spectra were taken as nujol or hexachlorobutadiene mulls between caesium iodide or caesium bromide plates on a Beckman IR-12 infrared spectrophotometer. The spectrum of aniline was measured as a liquid film between caesium iodide plates. The spectrum of 4-methylaniline was measured in carbon tetrachloride or cyclohexane solution in a liquid cell with caesium bromide windows. The accuracy of the instrument is quoted as 0.2 cm^{-1} at 200 cm^{-1}, 0.3 cm^{-1} at 400 cm^{-1}, 0.4 cm^{-1} at 740 cm^{-1}, 0.6 cm^{-1} at 1330 cm^{-1} and 0.7 cm^{-1} at 2220 cm^{-1}. The repeatability of the instrument is quoted as 0.1 cm^{-1} at 200 cm^{-1}, 0.15 cm^{-1} at 400 cm^{-1}, 0.2 cm^{-1} at 740 cm^{-1}, 0.3 cm^{-1} at 1330 cm^{-1} and 0.35 cm^{-1} at 2220 cm^{-1}. The instrument was calibrated against carbon dioxide, water vapour and polystyrene film. For maximum precision the frequencies were read directly from the wavenumber drum. Spectra of the ^{15}N-labelled compounds and their unlabelled analogues were repeated at least five times. Reproducibility of frequencies of these compounds is better than 0.4 cm^{-1}.

(ii) Electronic spectra.

Electronic spectra were taken as dry solids on filter paper or nujol mulls between glass coverslips in the reflectance mode and in solution in the transmittance mode on a Beckman DK-2A ratio recording spectrophotometer. For wavelength measurements, the accuracy of the instrument is quoted as better than 0.4 nm in the ultraviolet and

1.5 nm in the visible spectrum and the reproducibility is quoted as better than 0.05 nm in the ultraviolet spectrum. The instrument was calibrated with a didymium filter.

(iii) Magnetic measurements.

Magnetic susceptibilities were determined at room temperature on a Newport-Stanton Gouy magnetic balance. The instrument was calibrated with mercury(II) tetrathiocyanatocobaltate. Accuracy was checked with copper(II) acetate (found: 1.45 BM at 295K; reported[237]: 1.40 BM at 293K), copper(II) acetylacetonate (found: 1.80 BM at 295K; reported[237]: 1.91 BM at 292K) and cobalt(II) acetate (found: 5.20 BM at 295K; reported[237]: 5.13 BM at 295K).

(iv) Microanalyses.

Microanalyses were performed by Mr. W.R.T.Hemsted and Dr. K.G. Fuhr of this department and by Dr. F. Pachler of Bonn, Germany.

2. PREPARATION OF COMPOUNDS.

(i) Metal halide aniline complexes.

The complexes were prepared by mixing ethanol solutions of the appropriate aniline and metal(II) halide. The resultant solids were filtered off and recrystallized from ethanol. ^{15}N-labelled compounds were prepared from ^{15}N-*p*-toluidine of 95 atom % isotopic purity supplied by Prochem Ltd. Microanalysis results are given in Table 1.

(ii) β-Ketoenolate compounds.

The β-ketoenolates were generally available commercially. Dipivaloylmethane was prepared[238] by the condensation of t-butyl methyl ketone with methyl t-butyrate. Benzoylacetanilide was prepared[239] by the condensation of aniline with ethylbenzoylacetate. Solutions, for the determination of electronic spectra, were made in methanol.

The solutions of the sodium salts of the β-ketoenolates were prepared from methanol solutions of the β-ketoenolates by adding a fifty-fold molar excess of sodium methylate.

The copper complexes were generally prepared by methods described in the literature[100,109,110,240-244]. The complexes of acetoacetanilide and benzoylacetanilide were prepared by mixing hot solutions of ligand and Cu(II) acetate in ethanol in 2:1 molar proportions and filtering off the resulting precipitate. Solutions, for the determination of electronic spectra, were made in methanol.

Methanol of E. Merck, Darmstadt, pro analysi grade was used for the preparation of the solutions. For those complexes, of which

electronic spectra have previously been reported in a wide range of solvents[103,105,109,110,136,138-140,155,245-255], the spectra determined in the present work yielded comparable wavelengths of absorption maxima, but considerable differences in intensity were observed in some cases.

(iii) Acetoacetanilide and benzoylacetanilide compounds.

The ligands were prepared[239] by condensation of anilines with ethylacetoacetate or ethylbenzoylacetate. The copper complexes were prepared by mixing hot solutions of ligand and Cu(II) acetate in methanol or ethanol in 2:1 molar proportions. The resultant precipitates were filtered off, washed and air dried. The methanol adducts were prepared by stirring a suspension of the solids in methanol and filtering off the resultant solid. The solutions of the sodium salts were prepared directly in methanol by adding an excess of sodium methylate to a solution of the ligand. Microanalysis results are given in Tables 2 to 4.

(iv) N-Salicylideneanthranilic acid compounds.

The ligands were prepared by gently heating the salicylaldehyde and anthranilic acid in ethanol and filtering off the resultant precipitate.

The complexes were prepared by stirring (whilst gently heating) equimolar proportions of ligand and Co(II), Ni(II), Cu(II) or Zn(II) acetate in methanol, distilled from anhydrous magnesium sulphate. The resulting solid was filtered off, air dried and heated under reduced pressure at about 110°C for 24 hours. The attempted preparation of monoammine complexes of Ni and Cu by reaction in the presence of ammonia[186,187] was not successful; hydrolysis of the ligand occurred

with production of a salicylaldimine or anthranilate complex.

^{15}N-labelled compounds were prepared from ^{15}N-anthranilic acid of 95 atom % isotopic purity supplied by Prochem Ltd.

Microanalysis results are given in Tables 5 to 7.

(v) Aroylarylidenehydrazone compounds.

The ligands were prepared[256] by the condensation of benzoic acid hydrazide, prepared by the reaction of hydrazine hydrate with ethyl benzoate, with the appropriate aldehyde.

The benzoylbenzilidenehydrazone complexes were prepared[205] by refluxing ethanolic solutions of ligand and Ni(II) or Cu(II) acetate and filtering off the resultant precipitate. The Ni(II) complexes were recrystallized from chloroform.

The bis(benzoylsalicylidenehydrazone) complexes were prepared[209] by heating, with stirring, benzoic acid hydrazide, the appropriate salicylaldehyde and Co(II), Ni(II) or Zn(II) acetate in 2:2:1 molar proportions in ethanol. The resultant precipitates were filtered off, air dried and then heated at about 120°C under reduced pressure for 24 hours. Preparation from the preformed ligand did not produce analytically pure compounds. Bis(benzoyl 3,5-dichlorosalicylidenehydrazone) copper(II) was prepared by mixture of hot ethanolic solutions of ligand and Cu(II) acetate and filtering off the resultant precipitate.

The benzoylsalicylidenehydrazone monoammine and α-diimine complexes were prepared[209,212,213] by mixing ethanolic solutions of

ligand, amine or α-diimine and Ni(II) or Cu(II) acetate and allowing to stand. The resultant precipitate was filtered off and air dried.

The benzoylsalicylidenehydrazone copper complexes were prepared by heating the appropriate monoammine complexes at about 130°C under reduced pressure for 24 hours.

Microanalysis results are given in Tables 8 to 13.

(vi) Formazan compounds.

The ligands were prepared by coupling benzenediazonium cations of the anilines with the appropriate compound as follows:

C-aryl and C-methyl formazans; with the phenylhydrazone of benzaldehyde or acetaldehyde, respectively, in 1:1 molar proportions[257].

C-H formazan; with malonic acid in 1:1 molar proportions[228].

C-nitro formazan; with nitromethane in 2:1 molar proportions[258].

C-cyano formazans; with ethylcyanoacetate in 2:1 molar proportions[232].

C-acetyl and C-ethoxycarbonyl formazan; with ethylacetoacetate under the appropriate conditions[226].

The Co and Ni complexes were prepared[219] by refluxing ligand and Co(II) or Ni(II) acetate in aqueous ethanol/acetone mixture. The resultant Ni complexes were washed successively with ethanol, 1M hydrochloric acid, water and ethanol. The resultant Co complexes were washed with ethanol.

The Cu complexes were prepared by stirring cold ethanol/ acetone solutions of ligand and Cu(II) acetate.

^{15}N-labelled compounds were prepared from ^{15}N-aniline of 95 atom % isotopic purity supplied by Prochem Ltd.

Microanalysis results are given in Tables 14 to 19.

III. RESULTS

1. ANALYSES OF COMPOUNDS

Table 1. Analytical data on the metal chloride aniline complexes

Complex	Calculated			Found		
	%C	%H	%N	%C	%H	%N
$CoCl_2(4\text{-}CH_3an)_2$	48.9	5.3	8.1	48.6	5.2	8.1
$NiCl_2(4\text{-}CH_3an)_2$	48.9	5.3	8.2	48.6	5.2	8.1
$CuCl_2(4\text{-}CH_3an)_2$	48.2	5.2	8.0	47.9	5.1	8.2
$ZnCl_2(4\text{-}CH_3an)_2$	48.0	5.2	8.0	47.7	5.2	7.9

Table 2. Analytical data on the copper benzoylacetanilide complexes $Cu(BzAc\ \ R\text{-}An)_2$

R	Calculated			Found		
	%C	%H	%N	%C	%H	%N
4-NO_2	57.2	3.5	8.9	56.6	3.4	8.8
4-CN	65.1	3.8	9.5	64.8	3.7	9.0
4-$COCH_3$	65.4	4.5	4.5	64.9	4.7	4.4
4-Br	51.6	3.2	4.0	51.7	3.1	4.2
4-Cl	59.2	3.6	4.6	58.7	3.7	4.7
4-F	62.6	3.9	4.9	62.8	3.9	4.6
H	66.7	4.5	5.2	66.4	4.4	5.4
4-$NHCOCH_3$	62.4	4.6	8.6	62.1	4.6	8.4
4-CH_3	67.7	5.0	4.9	67.2	4.9	4.8
4-OCH_3	64.0	4.7	4.7	63.7	4.4	4.5
3-NO_2	57.2	3.5	8.9	57.4	3.9	8.9
3-Br	51.6	3.2	4.0	51.8	3.3	4.1
3-Cl	59.2	3.6	4.6	59.2	3.5	4.5
3-I	45.2	2.8	3.5	45.6	2.6	3.6
3-F	62.6	3.9	4.9	62.6	3.6	4.8
3-OCH_3	64.0	4.7	4.7	64.0	4.7	4.7
3-CH_3	67.7	5.0	4.9	67.2	4.9	4.7
3,5-diBr	42.1	2.4	3.3	42.2	2.3	3.3
3-Cl,4-CH_3	60.3	4.1	4.4	60.5	4.2	4.3
3,4-diCH_3	68.5	5.4	4.7	68.2	5.4	4.8
4-C_6H_5	72.9	4.7	4.1	72.6	4.6	4.1

Table 3. Analytical data on the methanol adducts of the copper benzoylacetanilide complexes $Cu(BzAc\ R\text{-}An)_2(CH_3OH)_2$

R	Calculated			Found		
	%C	%H	%N	%C	%H	%N
3-Br	50.4	4.0	3.7	50.2	3.9	3.5
3-Cl	57.1	4.5	4.2	56.7	3.9	4.5
3-I	44.9	3.5	3.3	43.9	3.4	2.9
3-F	60.0	4.7	4.4	59.7	4.6	4.5
$3\text{-}OCH_3$	61.5	5.5	4.2	61.2	5.4	4.2
$3\text{-}CH_3$	64.6	5.7	4.4	63.9	5.6	4.4
$3\text{-Cl,4-}CH_3$	58.3	4.9	4.0	57.7	4.7	3.9
$3,4\text{-di}CH_3$	65.5	6.1	4.3	64.9	6.0	4.3

Table 4. Analytical data on the copper acetoacetanilide complexes $Cu(AcAcR\text{-}An)_2$

R	Calculated			Found		
	%C	%H	%N	%C	%H	%N
H	57.8	4.9	6.7	57.7	4.8	6.8
4-CH_3	59.5	5.5	6.3	59.1	5.5	6.4
4-OCH_3	55.5	5.1	5.9	54.6	5.0	5.9
3-NO_2	47.5	3.6	11.1	47.2	3.6	11.0
3-Br	41.9	3.2	4.9	41.8	3.2	4.8
3-Cl	49.5	3.8	5.8	49.3	3.7	5.8

Table 5. Analytical data on N-salicylideneanthranilic acid

	Calculated			Found		
	%C	%H	%N	%C	%H	%N
N-Salicylidene-anthranilic acid ^{14}N	69.7	4.6	5.8	69.9	4.5	5.9
N-Salicylidene-anthranilic acid ^{15}N	69.4	4.6	6.2	69.2	4.4	5.9

Table 6. Analytical data on the N-salicylideneanthranilate complexes M(R-salanth).

M	R	Calculated			Found		
		%C	%H	%N	%C	%H	%N
Co	H	56.4	3.0	4.7	56.1	3.1	4.7
Co	5-NO_2	49.0	2.4	8.2	48.3	2.4	8.1
Co	5-Cl	50.6	2.4	4.2	50.3	2.4	4.1
Co	5-CH_3	57.7	3.6	4.5	57.2	3.7	4.5
Co	3,5-diCl†	42.7	2.6	3.6	42.5	2.7	3.5
Co	3,5-diBr	36.9	1.6	3.1	36.4	1.7	3.1
Ni	H *	53.2	3.5	4.4	53.2	3.6	4.7
Ni	5-Cl *	48.0	2.9	4.0	48.2	2.8	4.3
Ni	5-CH_3 *	54.6	4.0	4.3	54.1	3.8	4.4
Ni	3,5-diCl*	43.7	2.4	3.6	43.2	2.5	3.7
Ni	3,5-diBr*	35.5	1.9	3.0	35.0	2.1	2.9
Cu	H	55.5	3.0	4.6	55.6	3.0	4.6
Cu	5-NO_2	48.4	2.3	8.1	48.0	2.6	7.9
Cu	5-Cl	49.9	2.4	4.2	49.6	2.4	4.1
Cu	5-CH_3	56.9	3.5	4.4	56.7	3.5	4.4
Cu	3,5-diCl§	44.2	2.1	3.7	44.5	2.8	3.5
Cu	3,5-diBr	36.5	1.5	3.0	36.3	1.7	2.9
Cu	3,5-diI	30.3	1.3	2.5	30.3	1.3	2.3
Zn	H	55.2	3.0	4.6	54.9	2.8	4.6
Zn	5-Cl	49.6	2.4	4.1	49.4	2.4	3.9
Zn	5-CH_3 §	55.0	3.7	4.3	54.8	3.6	4.6
Zn	3,5-diCl ↟	41.1	2.7	3.4	41.0	2.7	3.5
Zn	3,5-diBr †	34.4	2.1	2.9	34.5	2.1	2.7

§ hemihydrate

* monohydrate

† sesquihydrate

↟ dihydrate

Table 7. Analytical data on the N-salicylideneanthranilate complexes M(R-salanth)

M	R		Calculated			Found		
			%C	%H	%N	%C	%H	%N
Co	H	^{14}N	56.4	3.0	4.7	56.1	3.1	4.7
Co	H	^{15}N	56.2	3.0	5.0	55.7	2.8	4.5
Ni	H	^{14}N*	53.2	3.5	4.4	53.2	3.6	4.7
Ni	H	^{15}N*	53.1	3.5	4.7	52.4	3.9	4.7
Cu	H	^{14}N	55.5	3.0	4.6	55.6	3.0	4.6
Cu	H	^{15}N	55.4	3.0	4.9	54.7	3.0	4.8
Zn	H	^{14}N	55.2	3.0	4.6	54.9	2.8	4.6
Zn	H	^{15}N	55.0	3.0	4.9	54.6	2.9	4.5
Co	5-CH_3	^{14}N	57.7	3.6	4.5	57.2	3.7	4.5
Co	5-CH_3	^{15}N	57.5	3.6	4.8	56.8	3.5	4.8
Cu	5-CH_3	^{14}N	56.9	3.5	4.4	56.7	3.5	4.4
Cu	5-CH_3	^{15}N	56.7	3.5	4.7	56.2	3.4	4.6

* monohydrate

Table 8. Analytical data on the metal benzoylbenzilidenehydrazone complexes $M(BR\text{-}BH)_2$

M	R	Calculated			Found		
		%C	%H	%N	%C	%H	%N
Ni	H	66.3	4.8	11.1	66.2	4.3	10.8
Ni	4-CH_3	67.3	5.3	10.5	67.5	4.8	10.4
Ni	4-OCH_3	63.7	4.7	9.9	63.5	4.6	9.9
Cu	H	65.9	4.4	11.0	65.7	4.3	10.8
Cu	4-CH_3	66.7	5.2	10.4	67.0	4.9	10.3
Cu	4-OCH_3	63.2	4.6	9.8	63.2	4.6	9.9
Cu	4-$N(CH_3)_2$	64.5	5.4	14.1	64.4	5.5	14.2

Table 9. Analytical data on benzoylsalicylidenehydrazone

	Calculated			Found		
	%C	%H	%N	%C	%H	%N
Benzoylsalicylidene-hydrazone	70.0	5.1	11.7	69.8	5.0	11.6

Table 10. Analytical data on the bis(benzoylsalicylidenehydrazone) metal(II) complexes $M(BR\text{-}SH)_2$

M	R	Calculated			Found		
		%C	%H	%N	%C	%H	%N
Co	H†	60.5	4.4	10.1	60.9	4.4	10.3
Co	5-CH_3†	61.7	4.9	9.6	62.0	4.7	9.9
Co	5-Cl*	54.7	3.5	9.1	55.0	3.3	9.1
Co	3,5-diCl§	47.9	3.0	8.0	47.6	2.8	7.9
Ni	H *	61.6	4.3	10.3	61.4	4.1	10.4
Ni	3-OCH_3†	58.6	4.6	9.1	59.0	4.4	9.2
Ni	5-CH_3†	61.8	4.9	9.6	62.0	4.7	9.7
Ni	5-Cl*	54.5	3.8	9.1	54.7	3.4	9.2
Ni	3,5-diCl	49.8	2.7	8.3	49.4	2.7	8.1
Ni	3,5-diBr†	38.6	2.3	6.4	38.8	2.1	6.3
Ni	3,5-diI†	31.8	1.9	5.3	31.7	1.7	4.6
Cu	3,5-diCl	49.5	2.7	8.2	49.4	2.7	8.3
Zn	H *	60.8	4.2	10.1	60.8	3.7	10.3
Zn	3-OCH_3*	58.8	4.5	9.1	58.7	4.3	9.0
Zn	5-CH_3*	62.0	4.7	9.7	61.9	4.7	9.7
Zn	5-Cl*	53.9	3.7	8.9	53.7	3.4	8.6
Zn	3,5-diCl†	48.1	2.9	8.0	48.3	2.8	7.9

* hemihydrate
† hydrate
§ sesquihydrate

Table 11. Analytical data on the benzoylsalicylidenehydrazone ammine complexes $Cu(BR\text{-}SH)(NH_3)(H_2O)$

R	Calculated			Found		
	%C	%H	%N	%C	%H	%H
H	49.9	4.5	12.4	49.9	4.5	12.5
3-OCH_3	49.4	4.7	11.6	49.1	4.7	11.5
5-CH_3*	52.7	4.7	12.3	52.5	4.7	12.2
5-Cl§	47.0	3.5	10.8	47.3	3.5	10.7
3,5-diCl	41.0	3.4	10.1	41.4	3.2	10.4
3,5-diBr	34.0	2.7	8.5	33.4	2.9	7.8
3,5-diI	28.6	2.2	7.1	28.6	2.1	6.5

* hemihydrate

§ analyses as $CuL.(NH_3)_{\frac{3}{4}} . (H_2O)_{\frac{1}{2}}$ (Three preparations)

Table 12 Analytical data on the copper benzoylsalicylidenehydrazone 2,2'-bipyridine (bipy) and 1,10-phenanthroline (phen) complexes. Cu(BR-SH)(N-N)

R	(N-N)	Calculated			Found		
		%C	%H	%N	%C	%H	%N
H	bipy	62.9	4.0	12.2	62.5	4.0	12.1
3-OCH_3	bipy	61.5	4.1	11.5	61.3	4.0	11.4
5-Cl	bipy	58.5	3.5	11.4	58.3	3.4	11.2
3,5-diCl	bipy	54.7	3.1	10.6	54.8	3.0	10.6
3,5-diBr	bipy	46.8	2.6	9.1	46.6	2.5	9.0
3,5-diI	bipy	40.6	2.3	7.9	40.2	2.1	8.0
H	phen	64.1	3.7	11.9	64.7	3.7	11.5
3-OCH_3	phen	63.1	4.3	10.9	63.0	3.8	11.3
5-Cl	phen	60.8	3.7	10.8	60.3	3.4	10.9
3,5-diCl	phen	56.5	3.3	10.1	55.5	3.1	10.0
3,5-diBr	phen	48.8	2.5	8.8	48.5	2.7	8.7
3,5-diI	phen	42.6	2.2	7.6	42.0	2.1	7.5

Table 13. Analytical data on the copper benzoylsalicylidenehydrazone complexes $Cu_2(BR\text{-}SH)_2$

R	Calculated			Found		
	%C	%H	%N	%C	%H	%N
H	55.7	3.4	9.3	55.4	3.4	9.2
3-OCH_3*	52.9	3.9	8.2	52.7	3.8	8.3
5-Cl	50.0	2.7	8.3	50.0	2.8	8.3
3,5-diCl*	44.3	2.4	7.4	44.3	2.4	7.6
3,5-diBr	36.6	1.8	6.1	35.8	2.0	6.2
3,5-diI	30.4	1.5	5.1	29.7	1.7	5.2

* hemihydrate

Table 14. Analytical data on 1,3,5-triphenylformazan.

	Calculated			Found		
	%C	%H	%N	%C	%H	%N
1,3,5-Triphenyl-formazan ^{14}N	76.0	5.4	18.7	75.7	5.3	18.5
1,3,5-Triphenyl-formazan ^{15}N	75.7	5.4	18.9	76.6	5.5	17.5

Table 15. Analytical data on the 1,3,5-triphenylformazan complexes

M		Calculated			Found		
		%C	%H	%N	%C	%H	%N
Co	^{14}N	69.4	4.6	17.0	69.1	4.6	17.0
Co	^{15}N	69.2	4.6	17.3	69.0	4.5	17.0
Ni	^{14}N	69.4	4.6	17.1	68.9	4.6	17.3
Ni	^{15}N	69.2	4.6	17.3	69.3	4.6	16.9
Cu	^{14}N	68.9	4.6	16.9	68.7	4.7	16.9
Cu	^{15}N	68.7	4.6	17.2	69.0	4.5	17.0

Table 16. Analytical data on the 1-Rphenyl-3,5-diphenyl formazan complexes

M	R	Calculated			Found		
		%C	%H	%N	%C	%H	%N
Ni	H	69.4	4.6	17.1	68.9	4.6	17.3
Ni	4-NO_2	61.1	3.8	18.5	61.1	3.8	18.8
Ni	4-CN	67.9	4.0	19.8	68.2	4.0	19.7
Ni	4-$COOC_2H_5$	65.9	4.8	14.0	65.8	4.8	13.8
Ni	4-Cl	62.8	3.9	15.4	62.7	3.9	15.3
Ni	4-Br	56.0	3.5	13.8	56.0	3.4	13.6
Ni	4-I	50.2	3.1	12.3	50.9	3.1	13.0
Ni	4-F	65.8	4.1	16.2	64.9	4.1	15.6
Ni	4-C_6H_5	74.2	4.7	13.8	74.0	4.7	13.5
Ni	4-CH_3	70.1	5.0	16.4	70.2	4.9	16.2
Ni	4-OCH_3	67.0	4.8	15.6	66.8	4.7	15.4
Ni	4-OC_6H_5	71.4	4.6	13.3	71.4	4.5	13.2
Co	H	69.4	4.6	17.0	69.1	4.6	17.0
Co	4-Br	56.0	3.5	13.7	56.1	3.7	13.4
Co	4-F	65.8	4.1	16.2	65.8	4.0	16.0

Table 17. Analytical data on the nickel 1,5-diRphenyl,3-phenylformazan complexes

R	Calculated			Found		
	%C	%H	%N	%C	%H	%N
4-$COOC_2H_5$	63.5	4.9	11.9	63.4	5.0	11.4
4-Cl	57.4	3.3	14.1	57.0	3.2	13.9
4-CH_3	70.7	5.4	15.7	70.8	5.3	15.4
4-OCH_3	64.9	4.9	14.4	64.9	4.9	14.2

Table 18. Analytical data on the nickel 1,5-diphenyl,3-Rphenylformazan complexes

R	Calculated			Found		
	%C	%H	%N	%C	%H	%N
4-NO_2	61.1	3.8	18.5	62.0	3.9	18.5
4-Cl	62.8	3.9	15.4	63.2	3.9	15.2
4-C_6H_5	74.2	4.7	13.8	74.5	4.7	14.0
4-CH_3	70.1	5.0	16.4	69.8	5.0	16.1
4-OCH_3	67.0	4.8	15.6	67.1	4.7	15.5

Table 19. Analytical data on the nickel 1,5-diphenyl-3-R formazan complexes

R	Calculated			Found		
	%C	%H	%N	%C	%H	%N
$COCH_3$	61.6	4.5	19.0	61.6	4.5	18.2
$COOC_2H_5$	59.2	4.7	17.3	58.6	4.5	17.3
CN	60.6	3.6	25.2	60.6	3.5	24.3
H	61.8	4.4	22.2	61.5	4.2	21.2
NO_2	52.5	3.4	23.5	52.4	3.4	23.0
CH_3	63.1	4.9	21.0	63.0	5.0	20.7

2. INFRARED SPECTROSCOPIC RESULTS

All values are cm^{-1}.

Table 20. Vibrational frequencies and ^{15}N-induced shifts of 4-methylaniline (in carbon tetrachloride)

Frequency	^{15}N-induced shift ($\Delta\nu$)	Assignment
3486	-8.2	νN-H antisym.
3399	-4.4	νN-H sym.
1628	-2.2	δNH_2
1275	-4.0	νC-N
1181	0.0	
1126	-0.9	NH_2 twist
812*	-0.7	NH_2 wag
504	-0.4	

* in cyclohexane

Table 21. Vibrational frequencies (ν) and ^{15}N-induced shifts ($>1.5cm^{-1}$)($\Delta\nu$) of the complexes $MCl_2(4\text{-}CH_3an)_2$

M	Co(II)		Ni(II)		Cu(II)		Zn(II)		Assignment
	ν	$\Delta\nu$	ν	$\Delta\nu$	ν	$\Delta\nu$	ν	$\Delta\nu$	
	3280	-19	3322	-8	3300	-8	3274	-7	(νN-H
			3313	-7					(antisym.
	3236	-13	3253	-6	3234	-5	3231	-4	(νN-H
			3236	-5					(sym.
	3136	-11	3130*		3118	-13	3136	-6	νN-H Cl
	3031		3032		3033		3031		
	1617		1619		1614		1617		
	1591		1593		1594		1595		
	1582	-5.7	1587	-3.6	1567	12.0	1583	-5.1	(δNH_2
			1571	-4.6					(
	1520		1516		1514		1514		
	1513								
	1466				1472				
	1458		1456		1458		1459		
	1384		1380		1379		1377		
			1297						
			1253	-4.9					(
	1242*		1239	-2.7	1240*		1242	-6.7	(νC-N
	1223	-2.6	1225		1221		1224	-3.8	(
	1214		1209	-3.7			1215	-2.6	
	1182		1183		1182		1183		
			1164	-1.5	1149	-3.2	1149	-3.3	
			1117						
			1101						
	1097	-10.5	1062	-5.2	1093	-9.0	1101	-9.4	NH_2 twist
	1074				1048		1045		
			1030	-2.1	1022		1023		
			1019						
			966						
	953		951		964		954		
	936		929		937		937		
	929						930		
	825		841	-1.6	835		827		
	811		814		814	-5.6	814		
	737	-6.5	743	-6.1	743	-9.5	739	-6.0	NH_2 wag
	704		708		707	-3.5	705		
	663	-2.4	649	-1.5	685	-5.8	674	-7.0	NH_2 rock
			620	-3.6					
	636		607	-4.4	639		638		
	525	-1.7	525	-1.9	535	-4.1	528	-2.2	coupled νM-N
			519	-1.7	518	-3.8			
	475	-4.0	479	-4.0	488	-1.1	475	-5.0	coupled νM-N
	426	-1.7	414	-3.6	455	-7.7	423	-4.4	νM-N

Table 21.(continued)

M	Co(II)		Ni(II)		Cu(II)		Zn(II)		Assignment
	ν	Δν	ν	Δν	ν	Δν	ν	Δν	
	400	-2.9	387		388		399	-2.0	
	326				327	-3.5			
	316	-1.6	309	-2.2	308	-1.6	311		
	297		275	-1.5			298		
			240						

* weak and broad bands; frequency and shift cannot be determined precisely.

Table 22. Vibrational frequencies of the copper benzoylacetanilide complexes $Cu(BzAc\ 4\text{-}RAn)_2$

R	H	4-NO_2	4-CN	4-$COCH_3$	4-I	4-Cl	Assignment
	3402	3356	3333	3322	3389	3411	νN-H
		3248	3236				νN-H
			2226				νC≡N
				1661			νC=O
	1609	1632	1628	1626	1622	1622	
	1602	1609		1602			
	1592	1597	1589	1590	1591	1589	νC ═ O
	1577	1585	1576	1579	1585	1579	
			1572		1574	1562	
	1537	1541	1540	1533	1534	1535	νC ═ O
			1535				
	1506	1495	1518	1495	1503	1504	
	1486	1485	1487	1491	1483	1484	
	1435	1431		1431	1428	1429	
		1409	1413	1406	1391	1398	
				1362	1344	1350	
	1329	1332	1330	1330	1320	1324	
	1323				1314	1313	
	1305	1306	1306	1309	1293	1291	
		1285	1281	1278		1271	
	1235	1259	1257	1250	1241	1242	
	1203	1211	1206	1213	1209	1209	
		1193	1183			1185	
	1184	1182	1178	1186	1184	1179	
	1164	1156		1151			
		1128				1122	
	1115	1111		1116		1115	
						1091	
	1070	1069	1068	1070	1066	1071	
	1029	1034	1034	1032	1032	1032	
	1014	1018	1021	1019	1018	1017	
	998	1003	1002	1002	1000	1009	
	981					994	
	968			961	940	941	
	924					925	
	911	914	913	912	911	912	
	904						
		864					
	848	851	840	832	822	845	
	839	839		820	814	824	
	793	791	784	797			
	764					768	
	750	753	756	766	756	756	
	739		742				
	727	724	723	724	719	719	
		694				696	
	691	685	689	689	693	692	
		663	667	664	672	676	

Table 22. (continued)

R	H	4-NO_2	4-CN	4-$COCH_3$	4-I	4-Cl	Assignment
		636		636	629	641	
		627					
	620	620	620		620	629	
	582		565	591	590		
	554	571	555	567	569	571	
		535	548				
		501	512				
		496					
	510	457	485	496	501	505	νCu-O
		446	472	489		489	νCu-O
	483		451	450	452	460	
	466			436	433		
	415		409	406	404	392	
		387		373			
	320	330	325	327	335	296	
	280	291	281	287	282	284	
					229		
					215		

Table 22. (continued)

R	4-Br	4-F	4-$NHCOCH_3$	4-OC_6H_5	4-CH_3	4-OCH_3	Assignment
	3400	3431	3412	3399	3410	3328	νN-H
						3244	νN-H
			3295				νN-H
			1677				νC=O
			1661				
			1655				
	1623	1623	1620		1622	1625	
			1612				
				1605	1607		
	1589	1601	1604	1596	1593	1597	νC ═ O
	1578	1583	1569	1575	1578	1580	
			1560		1550	1551	
	1535	1541	1534	1540	1542	1541	νC ═ O
			1522		1516	1514	
	1506	1507	1518	1508		1507	
				1491			
	1483	1487	1487	1483		1483	
	1429			1429		1432	
	1393	1403	1405	1406	1403	1407	
	1347	1350					
	1322	1325	1320	1322	1322	1333	
	1312	1312					
	1294	1297	1285		1301		
	1270	1271		1273	1273	1273	
	1241	1243	1252	1250	1239	1240	
		1227	1212	1226	1218		
	1209	1205	1206	1205	1206	1206	
				1200			
	1180	1185	1180	1185		1177	
		1161		1174			
		1157	1157	1166		1155	
	1123				1130	1129	
		1116	1118	1118	1115	1122	
		1089					
	1073	1072	1068	1073	1070	1071	
			1043				
	1032	1032	1032		1032	1033	
			1022			1027	
	1016	1017	1013	1017	1017	1015	
	1003		1000		1002		
	991		967			971	
	940	932					
	924	929		921		924	
	912	912	912	911	911	912	
				901			
	846	855	856	874		856	
			838	836		830	
	821	830	824	817	818	807	
		805	795	794	798	791	

Table 22. (continued)

R	4-Br	4-F	4-$NHCOCH_3$	4-OC_6H_5	4-CH_3	4-OCH_3	Assignment
			775	761	791		
	756	755	757	752	761	760	
		737	751	732	735	743	
	719	717	715	727	724	732	
	694	697	689	692	698	699	
	674		678		674	667	
					664		
					654		
	631	634	646	645	641	637	
	622	619	627	616	619	624	
			623				
			604	604			
	571	572	550	574	577	569	
		547		548	551		
	503	525	527	517	530	550	νCu-O
	495	512	511		513	524	νCu-O
		485		491	485	502	
	455	455	459		472	466	
	437	418	428	424			
	405	405	402				
		384	360	392		388	
	346		341	341			
		315	302	321	301	328	
	284	283	282	283	279	285	
			262		250	241	
	230	226					
	220		218				

Table 22. (continued)

R	4-C_6H_5	Assignment
	3406	νN-H
	1603	
	1590	νC = O
	1581	
	1572	
	1536	νC = O
	1523	
	1496	
	1480	
	1445	
	1424	
	1403	
	1365	
	1324	
	1297	
	1272	
	1240	
	1206	
	1185	
	1158	
	1114	
	1070	
	1033	
	1014	
	1006	
	912	
	835	
	830	
	794	
	763	
	754	
	726	
	690	
	675	
	641	
	617	
	591	
	575	
	564	
	549	
	492	
	441	
	351	
	284	

Table 23. Vibrational frequencies of the copper benzoylacetanilide complexes $Cu(BzAc\ 3\text{-}RAn)_2$

R	3-NO_2	3-Br	3-Cl	3-I	3-F	3-OCH_3	3-CH_3	Assignment
	3406	3407	3409	3397	3402	3353	3406	νN-H
	1631	1609	1608	1606	1624	1633	1609	
	1589	1587	1589	1587	1599	1598	1592	νC ═ O
	1578	1570	1576	1569	1581	1582	1579	
	1547		1571		1561	1562		
	1535	1535	1535	1535	1542	1549	1541	νC ═ O
		1523	1522	1523		1517		
		1505	1507	1504			1508	
	1487		1491	1489	1485		1491	
	1431	1434	1421	1435	1439		1424	
	1424	1412		1406	1429			
	1354	1397		1391	1390			
	1331		1325		1334	1321	1325	
	1305	1312	1311	1312	1318	1310	1311	
					1309			
			1293		1294			
			1262		1275	1279		
	1247	1232	1245	1232	1254		1258	
	1222	1204	1209	1203	1210	1208	1213	
		1182		1183		1198		
	1184	1175	1185	1177	1187	1182	1189	
	1162	1156	1168	1157	1151	1164	1170	
	1120	1117	1117	1117	1111		1116	
	1105		1100	1100				
	1087	1099	1080		1089			
	1071	1074	1069	1069	1070	1052	1069	
	1036				1030	1030		
	1023	1019	1013	1016	1015	1019	1013	
					1002		1002	
	997	992		990	975	995	997	
	989	972		971	956			
		967						
	944	921	931	919	925	936	948	
	930	900		901		923	903	
	882		886		899	897	892	
	872	863	876	860	881			
	832	847	838	846	849	848		
	798	794		794	794		790	
	793	785						
		779	780	782	774		778	
	777	773	773	776			774	
	765	750	751	748	756	760	754	
		738		740	739	737		
	733		732	725	729	730	729	
		693	692	692	693	698		
	692	680	679	680	682	683	688	

Table 23. (continued)

R	3-NO_2	3-Br	3-Cl	3-I	3-F	3-OCH_3	3-CH_3	Assignment
	669	660		652				
	598		581			585	583	
	584	584	571	583	582	573	569	
		566	566					
	562	560	544	560	557	558	554	
	534	545	540		523			
	477	491						
	454	457	478	488	498	506	524	νCu-O
	426	436	442	456	458	459	479	νCu-O
		421	428	431	438	433	420	
				417	411	416		
		349	360	341			378	
		328		318	313	334		
	295	295	300	302			307	
	281	279	277	278	279	279	277	
						235		
	227		221	216	216	223	214	

Table 24. Vibrational frequencies of the copper benzoylacetanilide complexes $Cu(BzAc\ di\text{-}RAn)_2$

R	3,4-diCH_3	3-Cl,4-CH_3	3,5-diBr	Assignment
	3430	3414	3406	νN-H
	1622	1626	1609	
	1604			
	1593	1589	1585	νC ═ O
	1575	1578	1564	
	1564		1551	
	1554	1546	1532	νC ═ O
	1509	1503	1497	
	1484	1484	1485	
		1461		
	1455	1448	1442	
	1432	1422	1429	
	1406			
	1388	1384	1395	
	1372	1375		
			1344	
	1317	1305	1310	
			1288	
	1251	1243	1259	
			1235	
	1212	1208	1204	
	1185	1184	1185	
		1158		
	1114	1111	1110	
	1088			
	1072	1073	1070	
		1051		
		1032		
	1015	1017	1016	
	1000	1002	1002	
			986	
			970	
		935	938	
	923		921	
	903		889	
	892	887	884	
	839	832	853	
	817	823	835	
		793	796	
	755	753	751	
	743	739	740	
	735	722	730	
			700	
	693	689	690	
	682	660	676	
			665	
	621		619	
	575	599	587	

Table 24. (continued)

R	3,4-diCH_3	3-Cl,4-CH_3	3,5-diBr	Assignment
	558		573	
	541	569	559	
	516	509	532	
			490	
	485	495	468	νCu-O
	448	456	413	νCu-O
		446		
		439		
	412	411		
			382	
			319	
	282		278	

Table 25. Vibrational frequencies of the methanol adducts of the copper benzoylacetanilide complexes $Cu(BzAc\ 3\text{-}RAn)_2(CH_3OH)_2$

R	3-Br	3-Cl	3-I	3-F	3-OCH_3	3-CH_3	Assignment
	1635	1642	1642	1638	1633	1638	
	1605	1611	1608	1623		1609	
	1586	1590	1587	1599	1597	1594	νC ═══ O
		1577	1572	1581	1582	1580	
	1547	1556	1540	1550	1550	1551	νC ═══ O
		1542			1540	1541	
	1509	1519			1517	1517	
	1487		1489	1486	1488	1491	
	1410	1417	1406	1419	1421	1425	
						1407	
	1323	1328	1329	1330	1341	1321	
	1299	1309		1310			
	1291	1296	1304	1292	1321		
	1262				1282	1280	
	1248	1251	1246	1257	1258	1262	
					1227		
	1213	1215	1206	1210	1209	1216	
			1182				
	1167	1172	1177	1185	1198	1172	
				1150	1164	1158	
				1145			
	1111	1115	1111	1109	1114	1117	
	1090	1095	1091	1094	1089	1095	
		1080		1081	1071		
				1070			
	1073	1074	1070	1050	1052	1073	
	1031	1034	1036	1030	1030	1035	
					1020		
	1010	1010	1008	1013	1009	1025	
	999	1001	1000		1000		
	994	995	991	999	994	994	
	967	977	970	972		975	
				956	946		
	922	928	919	926	936	938	
					925	922	
				901	898		
	881	887		880	889	981	
		876		872	875	872	
		850		863	849	821	
	798	801	802	801	810	809	
	781	786		783	794		
		769	776	771		779	
	768	762	763	755	761	768	
			749	739	737	756	
	723	723	724	728	729	729	

Table 25. (continued)

R	3-Br	3-Cl	3-I	3-F	3-OCH_3	3-CH_3	Assignment
	694	700	695	693	697	700	
	678	680	680	679	684	691	
	665		657			677	
	620						
	579	582	579	580	586	594	
					575		
	555	559	557	558	567		
			541	522		522	
	489	496		508	503	501	
	472	472	483	479	477		
			456				
	432	437	425	450	455	477	νCu-O
		424		436		446	
	411	408			411	404	
				392	391	377	
	295	300	293	311	317	316	
	276	279	280	286	287	282	
			270	275	275		
	252	254	247	258		256	
		232			233		
	207			204			

Table 26. Vibrational frequencies of the methanol adducts of the copper benzoylacetanilide complexes $Cu(BzAc\ 3,4\text{-}diRAn)_2(CH_3OH)_2$

R	3,4-diCH_3	3-Cl,4-CH_3	Assignment
		1640	
		1624	
	1594	1591	νC = O
	1580	1576	
	1564		
	1555		νC = O
	1439	1490	
	1323	1309	
	1274	1286	
	1258	1264	
		1244	
	1219	1217	
		1207	
		1185	
	1127		
	1109	1113	
		1072	
		1051	
	1037	1034	
	1025	1015	
	996	1001	
	945	932	
	888	892	
	871	874	
	820	819	
		804	
	768	768	
		758	
		742	
	725	724	
	691	695	
	672	670	
	667		
	619		
	581	585	
	568	565	
		552	
	531	537	
		505	
	490	457	νCu-O
	462		
	445	437	

Table 26. (continued)

R	3,4-diCH_3	3-Cl,4-CH_3	Assignment
	430	413	
	405	389	
	361		
	319		
	287	288	

Table 27. Vibrational frequencies (ν) and ^{15}N-induced shifts (>1.5 cm^{-1})(Δν) of N-salicylideneanthranilic acid.

N-salicylideneanthranilic acid		Assignment
1690		νC=O
1620		νC=C
1599	-2.3	νC=N
1581		
1570	-2.2	νC=N
1459		
1392		
1366		
1294	-4.3	νC-N
1248		
1186		
1170		
1152		
1055		
945		
922		
875	-2.6	δC=N-C
852	-3.3	δC=N-C
813	-3.5	δC=N-C
805		
757		
703		
680		
590		
577		
548		
543		
535		
509	-1.8	
488		
459		
435		
393	-1.8	
333		
310		
267		
214		

Table 28. Vibrational frequencies (ν) and ^{15}N-induced shifts (>1.5 cm^{-1})(Δν) of the N-salicylideneanthranilate complexes M(salanth)

M	Co		Ni		Cu		Zn		
	ν	Δν	ν	Δν	ν	Δν	ν	Δν	Assignment
					1621	-1.8	1635	-11	νC=N
	1624	-7.8	1589	-7.9	1584	-8.0	1629	-13	νC=N
	1598		1601		1600		1598		
	1588						1585		
			1558		1561				
	1547		1543		1537		1546		νCOO
	1539		1539	-2.3			1540		
	1486				1484		1485		
	1470		1467	-4.1	1465		1469		
	1452								
	1445	-2.4	1446	-2.8	1442	-2.8	1450	-2.5	νC-N
	1406				1404		1412		
	1385	-6.3	1378	-7.8	1380	-8.4	1390	-7.9	νC-N
					1359				
	1337				1332		1339		
	1304		1298		1303		1306		νCOO
			1279		1276	-2.1	1273		
			1270						
	1255		1251		1251		1254		νC-O
	1231	-2.4	1221		1222	-1.8	1231	-3.3	νC-O
	1181		1180	-2.1	1192	-2.0	1180		
	1163						1163		
	1154		1153		1149		1154		
	1127		1128		1132		1128		
	1094		1097	-1.6	1098		1093		
	1041		1045	-1.6	1047		1042		
			1034		1028				
					980				
	975		987	-2.1	973		981		
	962				958	-1.9	959		
					951				
	924	-3.4	927	-3.4	932	-3.2	923	-3.3	δC=N-C
	882		873	-3.4	882	-2.4	878		δC=N-C
	849	-4.6	843	-4.2	856		848	-4.5	δC=N-C
			814	-6.4					
	797		795	-1.7	801		795		
	758				753		757		
	745		754		774		746		
			739		747		736		
			724						
	715		702		719		715		
	689		688		689		689		

Table 28. (continued)

M	Co		Ni		Cu		Zn		
	ν	Δν	ν	Δν	ν	Δν	ν	Δν	Assignment
			671						
			662						
	649		645		645		649		
					627				
	618	-1.6	607	-3.0	617	-1.7	612	-2.5	coupled νM-N
	603		590	-2.8			596		
	572				583		574		
	558		557		558		556		
	546		524				544		
					528	-1.5			νM-N
	500	-4.1	512		511	-3.6	502	-5.4	νM-N
	460		461		462		459		
	429		446				437		
			417		418		416		
			406		403				
	389	-3.1			372	-2.4	393	-1.6	coupled νM-N
	335		343		356		333		νM-O
					311				
	299		293		297		297		
					265				
	251				240		241		
	232				225				

Table 29. Vibrational frequencies (ν) and ^{15}N-induced shifts (>1.5 cm^{-1}) ($\Delta\nu$) of the N-5-methylsalicylideneanthranilate complexes M(5-CH_3 salanth)

M	Co		Cu		Assignment
	ν	$\Delta\nu$	ν	$\Delta\nu$	
	1625	-3.6	1575	-5.4	νC=N
	1597	-2.9	1610		νC=N
	1584		1592		
	1547		1540		νCOO
	1475		1485		
			1457		
	1451		1448		
	1409		1410		
			1401		
	1374	-4.0	1378	-7.4	νC-N
			1368	-4.3	νC-N
			1329		
	1299		1303		νCOO
			1286		
	1273	-2.0	1277		
	1259		1252		νC-O
	1228	-2.6	1226	-2.8	νC-O
	1206	-1.8	1204		
	1163		1174	-2.1	
			1164		
			1142		
			1136		
	1094		1098		
	1040		1047		
			1009		
	984	-2.7	981		
	955		956		
	944		949		
	888	-5.4	897	-7.4	δC=N-C
	874		880		
	863	-3.3	867	-4.0	δC=N-C
	820		818		
	809		805		
	762		779		
	762		758		
	734		737		
	720		719		
	693		696	-2.2	
	662		660		
	624	-2.5	632	-1.8	coupled νM-N
	591	-1.9	596		
	567		560		

Table 29. (continued)

M	Co		Cu		Assignment
	ν	Δν	ν	Δν	
	553		549		
	519	-3.4	531	-1.5	νM-N
	492		483		
	467		466		
	431	-2.0	455	-2.8	coupled νM-N
	415		409		
	400				
	358		359		
	350		347		
	335	-4.0	331		νM-O
			320		
	311		285		
			276	-2.8	
	264		247		
	224		212		

Table 30. Vibrational frequencies of the cobalt N-salicylideneanthranilate complexes Co(R-salanth)

R	H	5-NO_2	5-Cl	5-CH_3	3,5-diCl*	3,5-diBr	Assignment
	1624	1618	1618	1625	1623	1604	νC=N
	1598	1605	1596	1597	1592	1590	
	1588	1588	1586	1586	sh	1577	
		1557					
	1547	1530	1538	1549	1531	1514	νCOO
		1503					
	1486	1484	1485	1482	1486	1481	
	1470	1470	1464	1476			
	1452	1452	1451	1455	1449	1442	νC-N
	1445				1439		
			1415		1413		
	1406		1400	1413	1402	1423	
	1385	1393	1376	1375	1383	1395	νC-N
						1386	
	1337						
		1337					
	1304	1307	1299	1299	1305	1315	νCOO
				1272		1293	
	1255	1256	1251	1259		1275	νC-O
	1231	1216	1222	1227	1228	1229	νC-O
			1194	1206	1196	1193	
	1181	1184	1173	1163	1167	1156	
	1163	1166				1169	
	1154	1155					
	1127	1141	1138				
			1110			1116	
	1094	1107	1097	1094	1097	1098	
	1041	1046	1046	1040	1050	1052	
	975	990	980	983	981	986	
		968	964		971	965	
	962	953	958	955	960	953	
	924		936				
		911					
	882	894	887	888	885	884	
		884	870	874	867	861	
	849	870	859	863	852	845	
		840	827	820	815		
	797	802	806	809	811	808	
	758	766	765	774	776	769	
	745	754	760	762	757	752	
			734	733			
	715	727	728	719	731	729	
						718	
						710	
		702	705		703	705	
	689	666	674	692	660	658	
	649	655	658	662			

Table 30. (continued)

R	H	5-NO_2	5-Cl	5-CH_3	3,5-diCl*	3,5-diBr	Assignment
	618	627	623	623	635		coupled νM-N
	603			589		595	
	572	574	578		582		
	558	560	565	566	568	567	
	546	543	547	553	538	549	
		526			514	513	
	500	482	496	518			νM-N
				492	493	498	
	460	468	465	466			
	429	439	437	430	441	457	
			412	413	411	424	
	389	393	388	397		401	
			353	357	366	357	
		353		349	336	348	
	335	511	328	335			νM-O
						330	
	299	289	301	311	312	318	
	251	259	263	264	269	278	
	232	237	235	225		233	
		209	215				

* sesquihydrate

Table 31. Vibrational frequencies of the nickel N-salicylidene-anthranilate complexes Ni(R-salanth).H_2O

R H	5-Cl	5-CH_3	3,5-diCl	3,5-diBr	Assignment
		1618			
1601	1602	1601			
1589	1587	1589	1597	1599	νC=N
1558		1553	1565	1570	
1543	1559	1545			νCOO
1538					
				1513	
			1480	1481	
1467	1461	1473			
1446	1446	1448	1444	1440	νC-N
	1410	1411		1399	
1378	1384	1376	1366	1366	νC-N
	1375				
	1308	1314			
1298	1303	1300	1304	1304	νCOO
1279		1278			
1270					
1251	1248	1253			νC-O
1221	1217	1227	1229	1231	νC-O
		1215			
		1208			
1180		1201	1196	1198	
1153	1168	1165	1170	1157	
1128	1134	1139			
1097	1095	1096	1095	1095	
1045	1055	1050	1047	1039	
1034		1043	1044	1022	
		1043			
		1005			
987	985	988	980	974	
	976	980			
	959	970		953	
	951	953	959	950	
927	937				δC=N-C
873	882	890	881	878	δC=N-C
	875	877	863	866	
		867			
	851	855		850	
		840			
843	835	835	849	838	δC=N-C
813		814	807	807	
795	802	792	771	770	
754	754	757	755	753	
739	739	741	732	728	
725	724	724		709	
703		703	700	699	
688	670	688	663	661	

Table 31. (continued)

R H	5-Cl	5-CH_3	3,5-diCl	3,5-diBr	Assignment
671					
662					
645	654	656			
	617	614	627	626	
607	595	598	591	590	
590	585				
	561				
557	548	554	565	564	
		544	544	538	
524	521	522			
512					
		495	497	490	
461	466	461	458	461	
447	450	446			
	439	431	429	429	
416	415	420	424		
406				404	
	359			374	
343	347	355	354	343	
	321	337	313	321	
294	286	283	294	301	
	251	234	240	240	

Table 32. Vibrational frequencies of the copper N-salicylidene-anthranilate complexes Cu(R-salanth)

R	H	5-NO_2	5-Cl	5-CH_3	Assignment
	1621	1636	1636	1630	
	1600	1601	1608	1611	
	1584	1590	1584	1575	νC=N
	1561	1566	1565		
	1537	1544	1534	1540	νCOO
			1519		
	1484	1490	1485	1484	
		1479			
	1465	1464		1459	
	1442	1449	1450	1448	νC-N
		1437			
	1404	1411	1416	1409	
				1401	
	1380	1390	1383	1378	νC-N
	1359	1352		1368	
	1332	1343	1323	1329	
	1303			1303	νCOO
				1288	
	1276	1275	1270	1278	
	1251	1248	1242	1252	νC-O
	1222	1210	1211	1226	νC-O
			1193	1204	
	1192	1186	1174	1175	
	1149	1172	1161	1164	
	1132	1131	1133	1142	
				1135	
	1098	1108	1099	1098	
			1085		
	1047	1057	1055	1047	
	1028	1035		1012	
	980	997	996		
	973	985	979	981	
			968		
	959		953		
	951	954	948	956	
	932		939		δC=N-C
		902			
		897		897	
	882	883	883	880	δC=N-C
			879		
			866		
			860		
	856	860	853	867	
		840	824	818	
		811	809		
	801	801	804	806	
	774			779	
	753	761	763	758	

Table 32. (continued)

R	H	5-NO_2	5-Cl	5-CH_3	Assignment
	747				
	743	736	736	737	
	719	721	723	719	
	717				
	698	704	704	697	
		666	673	660	
	645	653	654		
	627	641	628	633	
	613				
	583	587	586	596	
	558	563	559	561	
		539	546	549	
	528				νM-N
	511	489	513	531	νM-N
				483	
	462			466	
		454	453	455	
	418	426	428		
	403	417	419	409	
			397		
	372	389	378	378	
	356	364	355	359	
				346	
		323	334	330	
	310		316	319	
	296	305		285	
	265		271	275	
	240	252	256	247	
	226		230	212	

Table 32 (continued)

R	3,5-diCl*	3,5-diBr	Assignment
		1637	
	1598	1596	
	1585	1587	νC=N
	1563	1568	
		1561	
	1539	1547	νCOO
		1501	
	1482	1482	
	1439	1444	νC-N
		1416	
	1396	1387	
	1385	1381	νC-N
	1327	1334	νCOO
		1270	
	1229	1230	νC-O
	1193	1188	
		1172	
	1166	1159	
	1156	1153	
		1116	
	1100	1096	
	1053	1052	
		1040	
	1019		
	976	980	
	965	963	
	886	881	
	879	873	
	862	866	
		853	
	846	843	
	809	810	
	775	765	
	758	755	
	733	718	
		706	
	708	700	
		671	
	663	659	
		644	
	597	590	
	573	569	
		552	
	540	541	
		515	
	505	491	
	461	452	
	430	418	
	431	424	
	392	401	

Table 32. (continued)

R	3,5-diCl*	3,5-diBr	Assignment
	362	367	
	333	328	
		309	
	285	274	
	272		
	250	248	
		238	

* hemihydrate

Table 33. Vibrational frequencies of the zinc N-salicylideneanthranilate complexes Zn(R-salanth)

R	H	5-Cl	5-CH_3*	3,5-diCl†	3,5-diBr§	Assignment
	1635	1624	1624	1628	1625	νC=N
	1629					
	1599	1596	1596	1593	1593	
	1585	1582	1585	1588	1583	
	1547				1557	
	1540	1540	1546	1543	1539	νCOO
				1520	1508	
	1485	1484		1485	1484	
	1469	1464	1475		1450	
	1450	1446	1450	1440	1434	νC-N
		1418		1415	1412	
	1411	1403	1409	1405	1401	
	1390	1379	1379	1386	1382	νC-N
	1340		1340			
	1306	1301	1303	1306	1310	νCOO
	1273		1272			
	1254	1250	1256			νC-O
			1240			
	1231	1218	1226	1227	1229	νC-O
	1180	1191	1207	1196	1197	
	1164	1171	1166	1164	1150	
	1155		1154		1166	
	1129	1139				
		1108				
	1094	1095	1095	1096	1096	
			1068			
			1050			
	1043	1046	1042	1049	1050	
			989	983	984	
	982	988	982	971	962	
	960	959	953	960	949	
	924		935			
	878	883	888	883	883	
		869	874	868	866	
	848	854	860	849	854	
		822	831		837	
		812	819	816	816	
	795	801	807	812	810	
				776	773	
	757	763	762	758	754	
	745	728	738	730	728	
	736		734		712	
	715	707	717	703	700	
	689	671	690			
	649	655	661	660	658	
	612	618	618			coupled νM-N
	596					

Table 33. (continued)

R	H	5-Cl	5-CH_3*	3,5-diCl†	3,5-diBr§	Assignment
	575	578	587	584	583	
	556	564	568	567	564	
	544	544	549	538	534	
			544			
	502	500	514			νM-N
				515	511	
			487		481	
	459	466	467			
	437	440	436	441	444	
	416		420			
	393	404	404	407	402	
		350	353		380	
	333	323	330	331	339	νM-O
	297	294	307	309	308	
	241	248	249	262		
		219				

* hemihydrate

§ sesquihydrate

† dihydrate

Table 34. Vibrational frequencies of the nickel benzoylbenzilidene-hydrazone complexes $Ni(BR\text{-}BH)_2$

R	H	4-CH_3	4-OCH_3	Assignment
	1619			
	1609	1603	1612	
	1595	1594	1594	
	1588	1587	1587	
	1572	1564		
	1512	1523	1521	
		1503	1505	
	1488	1593	1590	
	1449	1455		
	1440	1440	1444	
	1402	1395	1397	
	1368	1369	1369	
	1316	1314	1316	
	1302	1303	1306	
	1296	1294		
			1258	
		1216	1212	
	1205	1202		
	1183	1183		
	1173	1174	1173	
		1165		
	1156	1156		
	1147			
	1140	1142	1142	
		1125		
	1101	1113	1115	
	1077			
	1069	1070	1070	
	1036	1034		
	1023	1023	1025	
	1002	1002		
	989			
	977			
	969	961		
	937	932	936	
		923		
	906	917	920	
	854		851	
	835	846	834	
		818		
	792	794	791	
		788		
	755	764		
		734	732	
	714			

Table 34. (continued)

R	H	4-CH_3	4-OCH_3	Assignment
	700	701	703	
	688	686	690	
	630	627	626	
	616	617	619	
	590	589	587	
	561		541	
	482	503	516	νM-N
		490		
	477	481	482	
			465	
	462	459	453	νM-O
	450			
	269	271	279	
		228		

Table 35. Vibrational spectra of the copper benzoylbenzilidene-hydrazone complexes $Cu(BR\text{-}BH)_2$

R	H	4-CH_3	4-OCH_3	4-$N(CH_3)_2$	Assignment
	1619	1631		1617	
	1609	1604	1602	1603	
	1596	1595	1593	1590	
	1586	1587		1584	
	1572	1568	1567	1554	
	1499	1506	1510	1522	
	1486	1490	1491	1490	
	1450		1461		
	1436	1438	1436	1440	
	1409	1415	1424	1414	
	1369	1382	1380	1377	
		1352	1346	1343	
	1325			1329	
	1313	1315	1314		
	1304	1307	1306	1308	
	1297	1294	1296	1294	
			1264		
				1248	
		1222	1234	1235	
	1203	1191	1185	1192	
	1180	1177		1188	
	1170	1170	1171	1170	
	1157		1157	1140	
	1146	1139	1137	1135	
		1114			
	1101	1104			
	1074				
	1068	1071	1070	1070	
		1047			
	1035	1026	1037	1026	
	1022	1014	1014	1006	
	1001	1000	999	998	
	990		990	996	
	976				
	971	964	956	969	
		953		952	
	939	933	931	932	
			925	928	
	906				
	854	860	862	857	
	832	833	820	813	
	797	805	805	807	
		791	791	793	
		780	778	788	
	757			743	
		725	720	722	

Table 35. (continued)

R	H	4-CH_3	4-OCH_3	4-$N(CH_3)_2$	Assignment
	705	711	705	708	
		706			
		697		699	
	688			690	
		646	644	644	
	619	624	617	615	
	586	567	574	563	
		559	563	557	
		529	533	532	
	545	512	525	517	
			495		
	467	470	477	481	νM-N
	441	438	425	409	νM-O
	411	396	385	381	
			425	426	
			415		
		407	404	407	
		387			
		356	362	355	
		348	351		
	290	291	289	290	
	241	261	264		
		225	219	233	

Table 36. Vibrational frequencies of benzoylsalicylidenehydrazone

Benzoylsalicylidenehydrazone	Assignment
3450	(
3360	(νO-H
3218	(and
3183	(νN-H
1657	νC=O
1630	
1621	
1607	
1576	
1495	
1488	
1445	
1415	
1403	
1356	
1346	
1326	
1311	
1303	
1273	
1244	
1219	
1203	
1164	
1150	
1095	
1072	
1035	
1001	
969	
965	
930	
923	
876	
852	
843	
804	
784	
756	
739	
700	
686	
577	
552	
478	
425	
386	
294	

Table 37. Vibrational frequencies of the cobalt benzoylsalicylidene-hydrazone complexes $Co(BR\text{-}SH)_2$

R	H†	5-CH_3†	5-Cl*	3,5-diCl§	Assignment
		1620		1618	
	1602	1601	1605	1605	νC=N
	1569	1566	1571	1570	
	1535	1544	1556	1552	
	1506	1509	1528	1518	
	1492	1493	1495	1493	
	1464	1468	1460		
	1435			1433	
		1412	1408	1410	
	1374	1374	1372	1383	νC-N
	1330		1344		
		1317	1315		
	1303	1302	1305	1308	νC-O
	1295	1292		1293	
		1259	1249		
		1223			
		1212		1212	
	1189	1170	1176	1165	
	1154	1146	1140		
	1127				
				1107	
	1097		1101	1099	
	1077	1091		1090	
	1040	1030	1031	1031	
	1003	1004	1002	1002	
				976	
	963				
	958	957	953	951	
			942		
	923	925		928	
	890	903	896	899	
				875	
	855		873	861	
				839	
		816	816		
	785	797	788	795	
	757			754	
	737	737	733		
			724		
	699	700	700	706	
	689	690		686	
		672			
	645	639	655		
	620	619	619	614	

Table 37. (continued)

R	H†	5-CH_3†	5-Cl*	3,5-diCl§	Assignment
	590	599			
	561	558	555	558	
	552	549			
	532		539	530	
		497			
		492			
	473	472	477	482	νM-L
	443	444	445	444	
	434	428	428	421	
			403	417	
	367	370		382	
	345	342	353	359	
	322	300	297	310	νM-L
	280				
	255	261	258	251	
		228		220	

* hemihydrate

† monohydrate

§ sesquihydrate

Table 38. Vibrational frequencies of the nickel benzoylsalicylidene-hydrazone complexes $Ni(BR\text{-}SH)_2$

R	H*	3-OCH_3†	5-CH_3†	5-Cl*	3,5-diCl	3,5-diBr†	3,5-diI†	Assignment
	1644	1645	1624	1622	1628	1629	1628	
	1605	1603	1601	1604	1602	1602	1605	νC=N
						1580		
	1568	1570	1565	1567	1565	1566	1569	
	1533	1539	1543	1529	1553	1552	1558	
					1517	1519	1519	
	1496	1496	1494	1493	1493	1491	1495	
	1464	1468	1468	1460				
	1438	1436		1441	1434	1427	1417	
		1390	1412	1413	1413	1407	1399	
	1379		1378	1375	1390	1382	1381	νC-N
	1338	1352	1342		1341	1340	1333	
		1322			1319			
	1313	1315	1321	1319	1308	1307	1310	νC-O
	1301		1298	1301	1294	1294		
	1256		1258	1249				
		1237						δO-C-O
		1215	1224					
		1208	1210	1213	1211	1218	1223	
		1175	1171	1176			1187	
	1154	1147	1147		1162	1150	1139	
	1126	1116		1111	1129		1124	
					1106			
	1081	1083	1098	1100	1099	1100	1099	
			1090	1086	1091	1089		
	1039	1035	1030	1030	1029	1028		
	1002	1001	1005	1003	1002	1002	1001	
	966	978	968	957	977			
	956	963	957	944	951	957	951	
	921	936	929		926	927	943	
	891	905	906	900	901	897	895	
		876	870	871	876	879	887	
	851				861	862	864	
	844	855	841	838	837	833		
			818	820			820	
		797	798	789	794	793	796	
	782	782	799					
	760	740			756	751	750	
	757				751			
	735	734	740	733		739	738	
	725			724		714	714	
	699	709	701	701	708	703	703	
	689	693	690	686	686	686	677	
			670	654			668	
	617	634				632	634	
	617	610	618	618	614		617	
	590	601				605	600	

Table 38. (continued)

R	H*	3-OCH_3†	5-CH_3†	5-Cl*	3,5-diCl	3,5-diBr†	3,5-diI†	Assignment
	571		577	578				
	550		558	551	556	549	544	
	533	531		545	540	539		
					527	520	517	
	481	492	477	482	491	488	487	νM-L
			489					
	445	448	448	448	448	443	445	
	436	432	429		429	427	432	
		410		400	411			
	373	388	374	375	386	370	389	
	363	360		368	362		357	
	340			341	347	344	349	
				333				
	330	339	307	302	315	323	300	νM-L
	287						283	
	266	255	266	263	253			
		244	238	242	227	230		

* hemihydrate

† monohydrate

§ sesquihydrate

Table 39. Vibrational spectrum of the copper benzoylsalicylidene-hydrazone complex $Cu(BR\text{-}SH)_2$

R	3,5-diCl	Assignment
	1648	νC=O
	1615	
	1598	νC=N
	1579	
	1553	
	1545	
	1516	
	1493	
	1453	
	1433	
	1412	
	1379	νC-N
	1322	
	1312	
	1305	νC-O
	1279	
	1266	
	1213	
	1210	
	1169	
	1160	
	1132	
	1107	
	1091	
	1036	
	1001	
	993	
	976	
	948	
	928	
	895	
	879	
	862	
	857	
	838	
	797	
	757	
	710	
	702	
	688	
	678	
	622	
	556	
	531	
	521	

Table 39. (continued)

R	3,5-diCl	Assignment
	510	νM-L
	483	
	451	
	438	
	433	
	408	
	400	
	385	
	380	
	369	
	347	
	317	νM-L
	290	
	257	
	220	

Table 40. Vibrational frequencies of the zinc benzoylsalicylidene-hydrazone complexes $Zn(BR\text{-}SH)_2$

R	H*	3-OCH_3*	5-CH_3*	5-Cl*	3,5-diCl†	Assignment
	1625	1627	1622	1623	1622	
	1610	1608	1607	1611	1612	νC=N
	1573	1574	1571	1574	1574	
	1557	1559	1558	1553	1549	
	1535	1541	1540	1530	1520	
	1495	1495	1494	1492	1492	
	1464	1466	1469	1460		
	1439	1441			1437	
			1411	1412	1411	
	1384	1386	1378	1379	1389	νC-N
	1340		1340		1339	
		1328				
	1311	1314	1313	1312	1318	
		1305	1305	1305	1306	νC-O
	1299		1299	1297	1289	
	1253	1236	1259	1248		
		1216	1225			
	1190	1206	1210	1214	1213	
	1154	1171	1169	1177	1166	
		1149	1143	1151		
	1127	1115			1130	
	1084	1079		1100	1108	
					1098	
					1090	
	1039	1037	1031	1029	1030	
	1003	1002	1004	1004	1001	
	968	978	973	968	977	
	962	962	964	958	958	
		935	956	944		
	921	927	929	926	928	
	890	901	904	895	898	
					876	
		856	871	869	862	
	847				838	
			818	814		
	802	797	799	790	795	
	787	782				
					762	
	753				754	
	738	734	741	724		
	699	705	700	699	706	
	699	689	689	689	686	
			671	653		
	618	638	619	618	611	
		601				

Table 40. (continued)

R	H*	3-OCH_3*	5-CH_3*	5-Cl*	3,5-diCl†	Assignment
	589	588				
		576		562		
	554		562	551	558	
	524	521	543	530	530	
	490					
		478	489	484		
	470	469	469	471	480	νM-L
	443	438	446	442	442	
	423	428	419	419	419	
		398		399		
	366		365	348	358	
	337	331	313			
	309	303	295	286	301	νM-L
	251	244			242	
	244					
			219	226		

* hemihydrate

† monohydrate

Table 41. Vibrational frequencies of the copper benzoylsalicylidene-hydrazone ammine complexes $Cu(BR\text{-}SH)(NH_3)(H_2O)$

R H	3-OCH_3	5-CH_3*	5-Cl§	3,5-diCl	3,5-diBr	3,5-diI	Assignment
	3370	3384	3376	3372			(νN-H
3296	3306	3324	3299	3341		3302	(or
3160	3171		3170	3175			(νO-H
1615	1612	1620	1621	1612	1612	1606	
1600	1598	1597	1598		1599	1595	
	1587			1588	1588	1588	
	1561				1579	1566	
1537	1539	1532	1532	1521			
1514	1511	1508	1505	1502	1512	1500	
1495		1496		1493	1495	1489	
1483		1487	1483				
1469	1466	1469					
1445	1446	1454	1446	1441	1443	1436	
1440	1435	1440					
1381	1385	1377	1382	1385	1377	1370	
	1369	1368		1371	1360	1361	
1359		1348					
1338	1344		1351				
			1315		1310	1314	
1309	1311	1311	1307	1308	1307	1307	
1299	1297	1291	1294	1296	1300		
		1257	1282				
1237	1239	1235	1249	1250	1254		
1200	1216	1216	1226	1212	1217	1223	
1166	1175	1172	1185	1177	1165	1154	
1153	1167	1151	1154				
	1146	1139	1139				
1131	1124				1124	1116	
	1107		1098	1109	1098		
1079	1077	1072	1071	1072	1073	1074	
	1070						
1055	1045	1054	1048	1054	1060	1049	
1036	1030	1024	1024	1029	1027		
1027							
1003	1003	1012	1002	1003	1003	1004	
992	989		989				
978	972	967	970	975	974		
961	954	959	946	949	949	951	
938	933	932	928	928	933		
900	919	917	903	919	913	904	
		884		882	888		
	869				879	868	
862	858	854	870	869	871	857	
			847		842		
		822	824				
		812	818			814	

Table 41. (continued)

R H	3-OCH_3	5-CH_3*	5-Cl§	3,5-diCl	3,5-diBr	3,5-diI	Assignment
793	796	796	791	791	795	791	
		786					
762				760		750	
	745	743		754			
	738						
722			729	719	719	725	
708	709	713	706	708	709	705	
	700						
	691	691	690	690	690	686	
656	642	657	660	659		674	
			639	632			
627	619	621	620	620	627	624	
603	587	598	598	599			
	563	573	571	577	574	570	
		563	561				
555				565	554	543	νM-N
	545			536	530		
515	504	528	515	525	522	521	
493		485					
468	475		465	470	471		
455	453	457	455	457	456	455	
410	420		411				
395				433	410	402	νM-N
	406			398			
	392	389	380	385	389	382	
365	371	377					
		347	351	347	349	345	
332	343	323	332		332		
	315	311		311	310	315	
292	302		300			305	
264	266	279	270	267		288	
	237	227		233			

* hemihydrate

§ $Cu(BR\text{-}SH)(NH_3)_{\frac{3}{4}}(H_2O)_{\frac{1}{2}}$

Table 42. Vibrational frequencies of the copper benzoylsalicylidene-hydrazone 1,10-phenanthroline complexes Cu(BR-SH)(phen)

R	H	3-OCH_3	5-Cl	3,5-diCl	3,5-diBr	3,5-diI	Assignment
	1621	1622			1621	1621	
	1606	1606	1610	1608	1604	1607	
	1594	1595	1595	1596	1593	1593	
	1583	1584	1580	1584	1576	1579	
	1579	1578					
		1554				1564	
	1531	1530					
	1520						
	1513	1513	1514	1517	1514	1514	
	1498	1499	1499	1499	1497	1499	
						1488	
	1461	1463	1463				
	1444	1444	1447	1442	1442	1440	
	1433		1435			1430	
	1425	1424	1426	1429	1427	1427	
	1411		1420	1422	1405	1395	
	1373	1374	1372	1372	1374	1371	
	1353	1352	1359	1354	1357	1356	
	1340	1341	1343		1343	1342	
	1315	1314	1324	1316	1316	1319	
	1302	1304	1308	1307	1307	1303	
	1294	1295	1299	1298	1294	1293	
		1279		1266	1271		
		1255	1257				
	1240	1240	1237				
	1216	1217	1222	1212	1206	1214	
	1206	1207					
	1194	1194	1178	1175	1156	1151	
	1169	1169		1170		1167	
	1156		1155				
	1144	1144	1140	1144	1140	1138	
	1136	1137					
	1120	1121				1112	
	1102	1102	1102	1104	1102	1101	
	1086	1086	1087	1090	1090	1087	
	1069	1069	1068	1070	1069	1068	
	1052	1051	1045	1052	1048	1045	
	1023	1024	1026	1025	1025	1026	
	1003	1003	1001	1003	1002	1001	
	990	992		990	991		
	974	975	967	970	985	983	
		959	955	945	959	961	
	952	952	946		943	943	
	929	929	928				
	897	897	906	910	906	901	
	890				883	889	

Table 42. (continued)

R	H	3-OCH_3	5-Cl	3,5-diCl	3,5-diBr	3,5-diI	Assignment
	867	866	865	868	865	864	
	854	854	853	857	854	853	
	848	849	848	846	847	845	
	829		830		829		
	806			802			
	796	795	796	797	797	798	
	780	780	780	776	775	774	
	760	760		759	754	752	
				754			
	744	744				752	
	733	732	729	727	731	728	
	728	728	719		727	720	
	712	712	711	716	719	711	
	697	698				707	
	691	691	692	693			
			684	682	678	683	
	650	662	658			672	
	640	640	640	643	641	641	
		619	621	623	620	615	
	603	605		608	607	607	
	586	586	591	579			
	538	538	558	551	559	560	
				537	531	525	
	505	506	514	512	514	509	
	488	488	491				
	481	480	478	473	477	474	
	462	461	464				
	449	452	450	447	451	452	
			442		440	440	
	426	425	423		423	423	
	413		409	404		411	
	385			425	403	392	νM-N
				397			
		385	382	379	389		
	365	365		366	367		
			351	351	354	349	
	339	339	340		322		
	302	305	309	315	315	307	
						293	
	281	280	280	281	280	280	
	260	261		265	268	266	
	245	245			244		
	229	229	232	242	231		
					224	229	

Table 43. Vibrational frequencies of the copper benzoylsalicylidene-hydrazone 2,2'-bipyridine complexes Cu(BR-SH)(bipy)

R	H	3-OCH_3	5-Cl	3,5-diCl	3,5-diBr	3,5-diI	Assignment
	1625	1608	1616	1612	1612		
	1606	1602	1601	1602	1602	1603	
			1596	1596			
	1594	1595	1590	1593	1592	1592	
		1585	1586		1586		
	1577	1574	1575	1576	1575	1575	
	1567	1565	1565	1565	1565	1564	
	1530	1543	1524				
	1520	1521	1502	1497	1499	1496	
	1493	1490	1490	1489	1489	1492	
	1476	1477	1459		1471	1473	
	1441	1467	1436	1433	1440	1439	
			1416	1408	1417	1414	
						1397	
	1375	1383		1372	1370	1370	
	1353	1364	1366				
	1341	1340	1351	1353	1352	1354	
			1325				
	1314	1315	1318	1317	1317	1316	
	1310	1304	1313	1307	1312	1307	
		1300	1303	1299	1306	1303	
	1293				1296	1291	
			1251	1264	1264	1260	
	1247	1240	1239	1251	1250	1247	
	1192	1214	1194	1207	1211	1214	
	1183	1174			1167	1170	
	1168	1168	1179	1162	1151	1150	
	1159	1157	1154				
	1143	1142	1135				
	1119	1110	1114			1111	
	1101		1099	1100	1101	1099	
	1077	1085	1088			1088	
	1068	1070	1074	1068	1067	1073	
	1062	1060	1065	1057	1058		
	1047	1038	1048	1041	1043	1043	
	1025	1024	1026	1026	1026	1027	
	1005	1007	1002	1011	1010	1007	
		989	986	980	980	989	
	976	974	972	976		978	
		966	967	965		970	
	949		952	942	950	954	
		938	935			936	
	931	930	923	936	939	928	
	898	916	905	909	904	900	
				879	880	885	
		873		866	866	865	

Table 43. (continued)

R	H	3-OCH_3	5-Cl	3,5-diCl	3,5-diBr	3,5-diI	Assignment
	860	853	854	852	851	853	
			845		833	834	
	811	819	813	813	813	809	
	796	795	792	796	795	794	
	791						
	767	776	765	765	765	765	
					763	759	
	746	740		746	750	754	
	735		737	735	735	735	
			727				
	713	713	705	714	715	713	
						709	
	697	697	695	693	696	692	
			688	683	678	685	
			683			670	
	657	654	655	656	655	655	
	650	638		651	652	653	
	627	628	625	629	629	629	
	605	616		623	617	614	
	583	583	591				
	543	555	549	562	555	554	
		542		534	526		
	506	505	511	515	510	509	
	487	470	492	472	469	468	
	462	452	463	458	458		
	448		448	447	445	449	
		439	439	440		440	
		421		425		422	
	417	414	421	417	417	415	
	405		407			407	
	385			406	389	397	νM-N
		392	382	391	384	378	
	368	371	356	377	370	367	
	356		347	363	356	341	
	338	339	336	321	325	310	
	301	302	315		314	299	
	250		276	269			
	231	244	234	238	242	239	
			222		234	222	
			205				

Table 44. Vibrational frequencies of the dimeric copper benzoylsalicylidenehydrazone complexes $Cu_2(BR\text{-}SH)_2$

R	H	3-OCH_3*	5-Cl	3,5-diCl*	3,5-diBr	3,5-diI	Assignment
	1625	1615	1625	1612	1609	1607	
	1599	1602	1598	1600	1598	1597	
	1587	1586	1587	1585	1584		
		1563				1568	
	1552	1544	1543				
	1513	1500	1510	1505	1502	1501	
	1492	1492	1492	1490	1488	1489	
	1481		1475				
	1447	1455					
	1441	1438	1442	1443	1441	1439	
			1409		1408	1403	
	1379	1385		1376	1374	1371	
		1362	1369				
	1343		1347				
	1303	1305	1304	1312		1308	
	1294	1297	1294	1306	1309	1304	
	1277		1268				
	1252	1257	1250				
		1247					
			1221				
	1209	1217	1201	1208	1212	1218	
	1174		1191				
	1166	1171	1178	1174	1163	1158	
			1170				
	1136	1146	1143				
	1129		1125		1123	1114	
		1108	1103	1105	1097	1092	
	1070	1081	1071	1074	1076	1076	
		1070					
	1042	1040	1048	1048	1050	1049	
	1026	1026	1024	1027	1028	1027	
	1001	1003	1000	1001	1003	1001	
	978		991		972	971	
	959	973	960	974	956	945	
			946				
	929	917	932	928	925		
	897		903			904	
	864	866	870	881	885	894	
	849	848	855	863	865	867	
			833			814	
	791	793	795	790	791	789	
		779					
	757			767	751	751	
		745	736	754			
		733	727	723	719	723	
	705	711	707	699	701	711	

Table 44 (continued)

R	H	3-OCH_3*	5-Cl	3,5-diCl*	3,5-diBr	3,5-diI	Assignment
	689	700	688		681	697	
						676	
	661	654	667				
	636	637	633	637	632	628	
	610	620	620	618	619		
	574	583	586	581	579	578	
		561	561	563			
		545	540		554	549	
	534			542	536	533	νM-N
		515		527	521	514	
	495	473	494	480	477	475	
	455	458	462	465	462	460	
		450	456				
	395			435	418	416	νM-N
			424	412			
			395				
		382	383		383		
	379		366	377		377	
	331	347	345	320	332	340	
	303	305			320	314	
		285	278	274		290	
	268	257	242	254	251	251	
			226				

* hemihydrate

Table 45. Vibrational frequencies and ^{15}N-induced shifts of 1,3,5-triphenylformazan.

Frequency	^{15}N-induced shift ($\Delta\nu$)	Assignment
1603		νC=C
1517		νC=N(+νN=N)
1509		νC=C
1499		
1459		
1449		νC=C
1355		νC-N
1317	-2.0	νC-N(exo)
1237	-2.0	νN=N(+νC=N)
1187	-2.3	νC-N(exo)
1181		
1164		
1157		
1150		
1126		
1100		
1074		
1046		νN-N(+νC-N)
1020	-1.6	νN-N
1003		
984	-2.0	δCNNC
918		
892		
847		
833		
821		
806	-2.2	δCNNC
764		
754		
738		
704		
692		
676		
653	-1.9	δCNNC
634		
618		
590	-2.6	δCNNC
570		
566		
545	-2.0	δCNNC
517		
502		
461		
278	-1.5	

Table 46. Vibrational frequencies (ν) and ^{15}N-induced shifts (>1.0cm^{-1}) (Δν) of M(1,3,5-triphenylformazan)$_2$

M	Co(II)		Ni(II)		Cu(II)		Assignment
	ν	Δν	ν	Δν	ν	Δν	
	1602		1603		1578		νC=C
	1591		1593		1586		νC=C
	1499		1501		1496		νC=C
	1484		1482		1483		νC=C
	1456		1457		1459		νC=C
	1375	-1.4	1403	-1.9			νC=N
			1334		1325		
	1311		1310		1309		
	1301		1298	-1.3	1300		
	1277		1285		1272		
	1242	-10.8	1270	-8.1	1232	d	νN=N
	1226	-5.3					νN=N
	1205						
	1192	-3.9	1204	-3.5	1185	-1.9	νC-N(exo)
	1176		1167		1160		
	1155		1159		1153		
			1090	-2.5			
	1075		1072		1079		
	1027		1027		1027	-2.6	
	1001		1006		1001	-1.0	
	991	-1.2	993	-1.7	986	-1.4	νN-N
			958				
					918		
	921	-3.0	916	-2.3	882	-5.9	δCNNC
	902		905		905		
	893		897	-1.3	878		
	851				846		
	844		832	-1.0	837		
	837		821		830		
					809		
	808	-2.4	813	-2.7	805		δCNNC
	774		767		772		
	759		753		754		
	694		688		691		
	683		682		688		
	676	-1.1	667		677		
					670		
	664		652		667		
	629	-1.9	638	-2.0	644	-2.6	
	620		620				
	615		617		617		
	584	-2.4	592	-1.6			
	574	-3.0	553	-3.0	611	-3.7	νM-N
					566		

Table 46. (continued)

M	Co(II)		Ni(II)		Cu(II)		Assignment
	ν	Δν	ν	Δν	ν	Δν	
	539	-1.4	525		522		
	507	-1.6			502		
	495		490		492		
			451				
	437	-1.0	430		433	-3.3	(νM-N
	415	-1.6	415	-3.0	415		(
			347		365		
			282				
	272		261		290		
	245		229		249		

d Band becomes a doublet at 1237 and 1250 cm^{-1} in the ^{15}N-labelled compound

Table 47. Vibration frequencies of the complexes Ni(1-Rphenyl, 3,5-diphenylformazan)$_2$

R	4-NO_2	4-CN	4-$COOC_2H_5$	4-Cl	4-Br	4-I	Assignment
	1603		1602	1605	1604	1604	
	1586	1597		1585	1585	1595	
				1576			
	1519		1509				
		1492	1496	1500	1500	1501	
	1484	1482	1481	1481	1480	1481	
						1476	
	1458	1461	1458	1459	1459	1458	
	1420	1420	1419				
	1414	1411		1412	1408	1403	νC=N
	1386	1386	1388	1388	1388		
			1367				
	1338	1344	1345	1339	1340	1340	
		1314		1312	1312	1312	
	1312	1310	1312	1304	1304	1305	
	1303	1298		1291	1291	1290	
	1281	1288	1279	1280	1279	1276	
	1266	1253	1266	1262	1260	1261	νN=N
	1218						
	1204	1202	1203	1203	1202	1203	νC-N(exo)
			1173	1172	1171		
	1165	1164	1167	1165	1165	1167	
			1127				
	1104	1113	1109	1105	1105	1107	
	1082	1085	1084	1087	1087	1088	
				1074	1069	1057	
	1027	1025	1026	1027	1027	1028	
	1014	1011	1014	1007			
	1002	1003	1003	1003	1003	1003	
	993	990	996	991	991	991	
	962	970		967	967	966	
		951		939	938	939	
	919	915	920	912	912	912	
	906		908	907	907		
	856		858				
	848	838	833				
	822	824	825	828	825	822	
				820			
	816		815	814			
	765						
	760	769	773	764	765	763	
	749	758	759	755	755	755	
	706		696	707			
	791		789		799		
	686	688	683	685	684	684	
	659	667		662	656	653	

Table 47. (continued)

R	4-NO_2	4-Cl	4-$COOC_2H_5$	4-Cl	4-Br	4-I	Assignment
	649	647	653	643	643	642	
	633		634	634	630	629	
	616	616	616	616	617	616	
	602	606	600	603	599	597	
		566					
	559	554	559	557	553	552	
	537						
	526						
	515	511	533	529	525	524	νM-N
			523				
			508	508			
	490	498	497	495	492	492	
	461		457	471	465	461	
	437	445	439	443	436	433	
				432			
	420		409	408	406	405	
	404	390			391		
	344	363	365	367	373	366	
			347			322	
	298		302	317	307	296	
	277	272	279	293	272	272	
		261					

Table 47. (continued)

R	4-F	4-C_6H_5	H	4-CH_3	4-OCH_3	4-OC_6H_5	Assignment
		1602	1604	1605	1602	1602	
	1598	1585	1595	1595	1585	1589	
		1568		1589			
	1509					1509	
	1496	1501	1502	1500	1500	1492	
	1483	1482	1482	1481	1482	1489	
	1458	1458	1457	1458	1459	1459	
					1442		
	1423			1421	1430	1417	
	1407	1412	1404			1400	νC=N
	1387	1388		1386	1396	1388	
	1343	1345	1335	1342	1346	1346	
		1330				1331	
	1312						
	1300	1311	1311	1312	1312	1314	
						1306	
	1290	1298	1299	1298	1302	1301	
	1283	1284	1285	1283	1285	1283	
	1272	1273	1270	1269	*	*	νN=N
	1234				1247	1246	
	1201	1206	1204	1205	1205	1203	νC-N
	1176			1176	1183	1176	
	1168	1167	1167	1167	1160	1165	
	1146			1158			
		1114		1111	1113	1101	
	1097		1090				
	1085	1086		1088	1088		
	1075	1077	1072	1075	1073	1077	
	1027	1029	1027	1028	1031	1029	
	1010		1006			1012	
	1003	1004	1000	1004	1004	1002	
	994	993	992	993	990	991	
	963	962	958	961			
	917	916	915	918	919	918	
	903	901	904	901		901	
			895			873	
		840	832	822		848	
	832	820	821	815	834	818	
	802		814			811	
	788					770	
	767	762	767	776		760	
	757	758	756	761	760	754	
		742					
	713	725		711		722	
						696	
	688	694	688	686	698	689	
	684	687	683	692	687	682	
	666	672		668	671	673	

Table 47. (continued)

R	4-F	4-C_6H_5	H	4-CH_3	4-OCH_3	4-OC_6H_5	Assignment
	653	651	652	648	647	650	
		642					
	639	630	637	643	641	638	
	618	617	620	614	616	616	
	609	594	593				
	574						
	560	561		549	552	548	
	545	542	554	576	577	581	νM-N
	524	531	525	522	530	523	
	513	510		515		515	
	492	491	490	489	498	500	
					480	484	
	465	454	452	454		464	
	450					451	
	425	419	431		439	421	
	409	412	415	414	414	415	
						406	
		387				371	
	349	360	349			345	
				319		321	
		279	282	293	292	286	
	264	261	259			259	

* Shoulder; precise frequency not able to be determined.

Table 48. Vibrational frequencies of the complexes Ni(1,5-Rphenyl,3-phenylformazan)$_2$

R	4-$COOC_2H_5$	4-Cl	4-CH_3	4-OCH_3	Assignment
	1601	1605	1604	1604	
	1584	1588	1585	1588	
		1576		1560	
			1518		
	1497	1501	1498	1500	
	1477	1479		1461	
	1457		1455	1457	
	1445			1440	
	1419	1413	1417	1425	νC=N
	1395		1396	1395	
	1338	1339	1345	1344	
	1308	1309	1312	1311	
	1287	1293	1298		
	1277	1276	1280	1288	νN=N
	1258	1262	1268		
				1252	
				1239	
	1201	1203	1205	1208	νC-N
			1173	1180	
	1166	1162	1160	1159	
	1125				
	1107	1102	1110	1110	
	1082	1091	1083	1083	
			1076	1075	
			1042	1048	
	1028		1029	1027	
	1012	1008	1012	1007	
	1001	998	1001	1001	
	991	988	993	992	
	974				
	964	965	959		
		939	941	947	
		920		928	
	919	912	916	915	
	862				
	850			850	
	830	830	836	836	
	816	809	822	828	
			787	800	
				796	
	773		771	767	
	762	764	762	762	
		705	710		
	699	694	692	696	
	693	682	684	683	
	672		667		

Table 48. (continued)

R	4-$COOC_2H_5$	4-Cl	4-CH_3	4-OCH_3	Assignment
	669		659	658	
	652	645	647	646	
	638	640	639	634	
	630	630	632	628	
	613	616	615		
		591	601	598	
	530	531	561	567	νM-N
	565	567	547	546	
				533	
	512		519	524	
	499	500	507	509	
	469	488	485	488	
		453	452	465	
	445	442		445	
		431	422		
	411	415	412	418	
	371	372	383	364	
	306	313	322	338	
	272	295		292	
	261	257		260	
	235	236	213	235	

Table 49. Vibrational frequencies of the complexes Ni (3-Rphenyl,1,5-diphenylformazan)$_2$

R	4-NO_2	4-Cl	4-C_6H_5	4-CH_3	4-OCH_3	Assignment
			1611	1620	1620	
			1604	1614	1611	
	1595	1592	1591	1596	1595	
			1586	1587		
					1548	
	1512	1513		1520	1520	
	1496	1498		1502	1502	
			1490	1490	1494	
		1480	1481	1480	1481	
		1456	1455	1457	1454	
	1405		1401		1407	νC=N
	1330	1349	1346	1348	1344	
				1338		
	1309	1308	1314	1310	1308	
		1298	1296	1300		
	1286	1283	1287	1283	1285	
	1277	1268	1257	1269	1270	νN=N
	1250				1250	
	1202	1204	1203	1203	1205	νC-N
		1171		1177	1175	
	1166	1165	1166	1165	1171	
		1153	1160	1154		
	1110	1102	1111	1112	1114	
	1088	1093	1092	1087	1091	
	1076	1075	1075		1074	
	1037				1034	
	1022					
	1012	1013	1008			
	1002	1003	1002	1003	1003	
	995	991	991	992	991	
	963	961	963	957		
	921		918			
	912	907	910	904	907	
	897					
	856		851			
	837	831			841	
		821	828	821	823	
	810	812	815			
	779			783	783	
	765		770		770	
	759	766	761	764	760	
	751	757	749	756		
	712	717	733			
			701			
	688	686	690	686	687	

Table 49. (continued)

R	4-NO_2	4-Cl	4-C_6H_5	4-CH_3	4-OCH_3	Assignment
		681	680	681	681	
			661			
	656	648	649	655	656	
	639	641	637	642	639	
	632				627	
	616	618	618	619	615	
	592	592	593	591	592	
	571	575	561			
	545	546	553	550	552	νM-N
	524	524	526	521	528	
	498	500	506	510	514	
	468		457	487	466	
	450	450	445	456	447	
	422	429	414	438	436	
	409	412	401	410	402	
	353	368	375	370	382	
			341		356	
					320	
	293	280			308	
	271	269	260	279	259	
				257		
	229	228	227	239		
	218		214			

Table 50. Vibrational frequencies of the complexes M(1-Rphenyl,3,5-diphenylformazan)$_2$

R	4-F		4-Br		
M	Co(II)	Ni(II)	Co(II)	Ni(II)	Assignment
	1598	1598	1597	1603	
				1585	
		1509			
	1495	1496	1496	1499	
	1483	1483	1479	1480	
	1453	1438	1455	1459	
		1423			
		1407	1400	1406	
	1371	1387	1372	1388	
		1343		1338	
		1328			
		1312		1312	
		1300		1304	
	1287	1290	1284	1291	
	1274	1283	1273	1279	
	1246	1272	1239	1260	νN=N
	1225		1225		νN=N
		1234			
	1195				
	1187	1201	1191	1202	νC-N(exo)
	1178	1176	1170	1171	
		1168		1165	
	1157	1161	1155		
	1148	1146			
	1095	1097	1104	1105	
		1085		1087	
	1079	1075	1070	1069	
	1027	1027	1025	1027	
	1010	1010	1010		
	1001	1003	1001	1003	
	993	994	990	991	
		963		967	
	936			938	
	918	917	915	912	
	905	903	899	907	
	835	833	821	825	
	827				
	810	802	804		
		788			
	778	767		765	
	758	757	760	755	
	716	713	715	708	

Table 50. (continued)

R	4-F		4-Br		
M	Co(II)	Ni(II)	Co(II)	Ni(II)	Assignment
	690	688	691		
	684	684	688	684	
	670	666	664	656	
	660	653	643	643	
	639	639		630	
	617	618	621	617	
	601	609	617	599	
		574	580	553	
		560			
	566	545	545	525	νM-N
	538				
	523	524			
	508	513	507		
	496	492	498	492	
	470	465		465	
		450			
	433	425	428	436	
	411	409		406	
			385	388	
	355	350	367	371	
	271	261	280	279	
	245	242	263	259	
	209				

Table 51. Vibrational spectra of the complexes Ni(3-R,1,5-diphenylformazan)$_2$

R	CN	$COOC_2H_5$	$COCH_3$	NO_2	H	CH_3	Assignment
	2233						νC≡N
		1724	1683				νC=O
	1593	1587	1588	1589	1590	1593	
				1531			νNO_2
	1500	1509			1504		
	1483	1481	1480	1479	1483	1479	
					1467		
	1458	1457	1457	1458	1459	1452	
		1397		1407		1419	
	1382	1377			1377	1383	
			1366		1346		
				1357			νNO_2
					1330		
	1349	1339	1341	1281	1318	1267	(
	1321	1320	1306				(νN=N
					1307		
	1293	1305	1290	1317	1287	1307	
						1296	
				1260			
	1210	1216	1211		1205	1214	
	1194				1183		
	1176	1176	1165	1173	1164	1164	
	1160	1161	1156	1163		1158	
		1141	1114	1149			
	1081	1095					
		1074	1073	1075	1075	1079	
						1049	
	1030	1032	1022	1025	1032	1025	
	1026			1018	1017	1006	
		1009	1010			1000	
	1000	1000	1001	998	1000	992	
	985				964		
	963	963	957	967	957	965	
	926				936		
	915	920	920	917	916		
	907	901		907	905	905	
		881		870	899		
	843	861			844	854	
	828	832	834		828	827	
		825	824	826	823		
		802	815				
	772	772		776	769		
	764	758	767	763	761	760	
				734	745		
	693	689	690	690	693	689	
	682	681	682	685	687	680	

Table 51. (Continued)

R	CN	$COOC_2H_5$	$COCH_3$	NO_2	H	CH_3	Assignment
		666	653		666	668	
	640	641	643	640	644	635	
			637		632		
	623	619		616	620	622	
	612	604	615	602	609		
		589	595		597		
	554	564	568				
	494	535	550	573	552	582	νM-N
	536	528	521		516	515	
	458	475	506	535	531	543	νM-N
					480		
			465	464	465	451	
	437						
	428	433	429	435	435	434	
	411			406	412	415	
					406	408	
					392		
	378	373		378	374		
	335	341	318	342	346	338	
	304			322			
	279	280	277	278	300	285	
		259					
	232	246	241	243	253	259	
		229		223	233	220	
	209		210		212		

3. ELECTRONIC SPECTROSCOPIC RESULTS.

Table 52 Electronic spectra of β-ketoenolates $R_1C(OH)CHCOR_2$ (in methanol solution)

R_1	R_2	Abbreviation	Transition Energy (kK)	Molar Absorptivity ($dm^3mol^{-1}cm^{-1}$)	Transition Energy (kK)	Molar Absorptivity ($dm^3mol^{-1}cm^{-1}$)
Alkyl substituents						
CH_3	CH_3	AA	36.8	7470		
$C(CH_3)_3$	$C(CH_3)_3$	DPM	36.4	9520		
CH_3	CF_3	TFA	35.1	2420		
CF_3	CF_3	HFA	32.9	1010		
CH_3	OC_2H_5	EAA	41.2	940		
CH_3	$N(C_2H_5)_2$	DEAA	39.2	4580		
Aryl substituents						
CH_3	C_6H_5	BA	32.5	16860	40.5	7080
C_6H_5	C_6H_5	DBM	29.3	26030	39.7	9740
CH_3	NHC_6H_5	AAA	41.2	17450		
C_6H_5	NHC_6H_5	BAA	32.2	8590	41.0	24720
C_6H_5	CF_3	BTA	30.7	7970	40.5	10650
C_4H_3S	CF_3	TTA	34.7	7920	38.0	10090
C_6H_5	OC_2H_5	EBA	35.0	3840	41.2	10450

Table 53. Electronic spectra of sodium β-ketoenolate salts ($R_1COCHCOR_2$)Na (in methanol solution)

R_1	R_2	Ligand Abbreviation	Transition Energy (kK)	Molar Absorptivity ($dm^3mol^{-1}cm^{-1}$)	Transition Energy (kK)	Molar Absorptivity ($dm^3mol^{-1}cm^{-1}$)
Alkyl substituents						
CH_3	CH_3	AA	34.1	20280		
$C(CH_3)_3$	$C(CH_3)_3$	DPM	36.0	8630		
CH_3	CF_3	TFA	34.1	19050		
CF_3	CF_3	HFA	33.1	2150		
CH_3	OC_2H_5	EAA	36.9	20680		
CH_3	$N(C_2H_5)_2$	DEAA	38.9	2110		
Aryl substituents						
CH_3	C_6H_5	BA	30.9	21180	42.0	10420
C_6H_5	C_6H_5	DBM	28.8	23100	41.8	14580
CH_3	NHC_6H_5	AAA	33.6	29530	41.3	15620
C_6H_5	NHC_6H_5	BAA	30.3	24540	39.9	13930
C_6H_5	CF_3	BTA	31.1	20420	41.8	9570
C_4H_3S	CF_3	TTA	29.9	17920	38.8	7640
C_6H_5	OC_2H_5	EBA	33.0	11500	43.7	10280

Table 54. Electronic spectra of copper(II) β-ketoenolate complexes $Cu(R_1COCHCOR_2)$ (in methanol solution)

R_1	R_2	Ligand Abbreviation	Transition Energy (kK)	Molar Absorptivity ($dm^3mol^{-1}cm^{-1}$)	Transition Energy (kK)	Molar Absorptivity ($dm^3mol^{-1}cm^{-1}$)
Alkyl substituents						
CH_3	CH_3	AA	34.3	25850	41.7	14510
$C(CH_3)_3$	$C(CH_3)_3$	DPM	33.7	21350	39.8	14770
CH_3	CF_3	TFA	33.9	20430	42.6	11050
CF_3	CF_3	HFA	32.8	21070	42.2	6360
CH_3	OC_2H_5	EAA	36.4	16530	44.4	8520
CH_3	$N(C_2H_5)_2$	DEAA	36.1	23160	42.6	13390
Aryl substituents						
CH_3	C_6H_5	BA	31.3	33800	39.1	26960
C_6H_5	C_6H_5	DBM*	28.7	40550	37.6	29780
CH_3	NHC_6H_5	AAA	34.1	47400	40.8	20320
C_6H_5	NHC_6H_5	BAA	30.8	46490	40.8	40590
C_6H_5	CF_3	BTA†	30.9	32120	36.9	24110
C_4H_3S	CF_3	TTA↑	32.0	42920	36.0	17270
C_6H_5	OC_2H_5	EBA	33.0	18560	41.5	24800

* in chloroform solution

† Additional band at 46.3 kK. Molar absorptivity 18570 $dm^3mol^{-1}cm^{-1}$

↑ Additional band near limit of measurement ~48 kK.

Table 55. Electronic spectra of the copper complexes of substituted benzoylacetanilides $Cu(BzAcRAn)_2$
(Reflectance spectra of solids on filter paper) (kK)

R	σ	*R*	$\pi_3 \rightarrow \pi_4^*$	$\sigma_L \rightarrow 3d_{xy}$
4-NO_2	0.78	0.16	25.8	34.0	41.3
4-CN	0.66	0.18	29.3	34.1	40.3
4-$COCH_3$	0.50	0.20	28.0	34.3	41.2
4-I	0.28	-0.20	29.7	(34)	39.2
4-Br	0.23	-0.18	29.9	(34)	39.4
4-Cl	0.23	-0.16	29.5	(34)	39.5
4-F	0.06	-0.34	30.5	(34)	40.5
H	0.00	0.00	30.5	(34)	40.7
4-$NHCOCH_3$	-0.01	-0.27	29.5	(37)	41.0
4-OC_6H_5	-0.03	-0.74	30.1	(34)	39.5
4-CH_3	-0.17	-0.14	30.0	(34)	40.3
4-OCH_3	-0.27	-0.50	29.7	(34)	40.3
3,5-diBr	0.78	-0.36	29.3	(34)	39.5
3-NO_2	0.71	0.16	29.7	(34)	40.0
3-Br	0.39	-0.18	30.0	(34)	40.8
3-Cl	0.37	-0.16	30.0	(34)	40.5
3-I	0.35	-0.20	29.9	(34)	41.2
3-F	0.34	-0.34	29.9	(34)	40.2
3-OCH_3	0.12	-0.50	29.9	(34)	40.5
3-CH_3	-0.07	-0.14	29.9	(34)	40.3
3,4-diCH_3	-0.24	-0.28	29.9	(34)	40.2
3-Cl,4-CH_3	0.20	-0.30	29.9	(34)	39.8

Parentheses denote shoulders.

Table 56. Electronic spectra of the complexes $Cu(BzAcRAn)_2$ (in methanol solution) (kK)

R	σ	*R*	$\pi_3 \rightarrow \pi_4$	$\sigma_L \rightarrow 3d_{xy}$	*d* → *d*
4-NO_2	0.78	0.16	25.8*	34.0*	41.3*	16.3*
4-CN	0.66	0.18	29.3*	34.1*	40.3*	15.9*
4-$COCH_3$	0.50	0.20	29.0	35.1	42.5	16.5*
4-I	0.28	-0.20	30.2	(35)	39.7	15.5
4-Br	0.23	-0.18	30.5	(35)	40.2	16.0†
4-Cl	0.23	-0.16	30.6	(35)	40.3	15.1†
4-F	0.06	-0.34	30.8	(35)	41.0	15.1
H	0.00	0.00	30.7	(35)	40.8	15.3
4-$NHCOCH_3$	-0.01	-0.27	30.1	(35)	38.8	15.6
4-OC_6H_5	-0.03	-0.74	30.5	(35)	40.3	15.6
4-CH_3	-0.17	-0.14	30.9	(35)	40.8	15.2
4-OCH_3	-0.27	-0.50	30.4	(35)	40.6	15.8
3,5-diBr	0.78	-0.36	30.2	(35)	42.2	15.5*
3-NO_2	0.71	0.16	30.3	(35)	40.5	16.7*
3-Br	0.39	-0.18	30.4	(35)	40.5	15.5†
3-Cl	0.37	-0.16	30.5	(35)	40.5	15.6†
3-I	0.35	-0.20	30.6	(35)	40.6	15.4†
3-F	0.34	-0.34	30.5	(35)	40.8	15.3
3-OCH_3	0.12	-0.50	30.5	(35)	40.8	15.3
3-CH_3	-0.07	-0.14	30.6	(35)	40.8	15.4
3,4-diCH_3	-0.24	-0.28	30.4	(35)	40.3	15.9†
3-Cl,4-CH_3	0.20	-0.30	30.3	(35)	40.2	15.6†

† In acetone (insufficiently soluble for measurement in methanol).

* Reflectance spectra of solid on filter paper (insufficiently soluble for measurement in solution).

Parentheses denote shoulders.

Table 57. Electronic spectra of the sodium salts of substituted benzoylacetanilides (in methanol solution) (kK)

R	σ	*R*	$\pi_3 \rightarrow \pi_4^*$	Benzenoid *p*-(^1L_a)
4-NO_2	0.78	0.16	26.3	42.4
4-CN	0.66	0.18	29.2	>50
4-$COCH_3$	0.50	0.20	28.3	43.1
4-I	0.28	-0.20	29.9	38.6
4-Br	0.23	-0.18	30.1	39.4
4-Cl	0.23	-0.16	30.1	39.4
4-F	0.06	-0.34	30.4	40.5
H	0.00	0.00	30.2	39.8
4-$NHCOCH_3$	-0.01	-0.27	29.8	37.6
4-OC_6H_5	-0.03	-0.74	30.0	39.4
4-CH_3	-0.17	-0.14	31.1	40.0
4-OCH_3	-0.27	-0.50	30.3	40.2
3,5-diBr	0.78	-0.36	29.9	39.1
3-NO_2	0.71	0.16	30.4	40.5
3-Br	0.39	-0.18	30.3	40.0
3-Cl	0.37	-0.16	30.1	39.5
3-I	0.35	-0.20	30.1	39.4
3-F	0.34	-0.34	30.3	39.8
3-OCH_3	0.12	-0.50	30.2	40.2
3-CH_3	-0.07	-0.14	30.3	40.2
3,4-diCH_3	-0.24	-0.28	30.3	40.2
3-Cl,4-CH_3	0.20	-0.30	30.2	39.8

Table 58. Electronic spectra of substituted benzoylacetanilides (in methanol solution) (kK)

R	σ	*R*	$\pi_3 \rightarrow \pi_4^*$	Benzenoid *p*-(^1L_a)
4-NO_2	0.78	0.16	30.4	44.0
4-CN	0.66	0.18	31.0	37.8
4-CH_3CO	0.50	0.20	30.4	33.5
4-I	0.28	-0.20	31.6	39.8
4-Br	0.23	-0.18	31.8	40.0
4-Cl	0.23	-0.16	31.7	40.1
4-F	0.06	-0.34	31.0	41.0
H	0.00	0.00	31.8	40.8
4-$NHCOCH_3$	-0.01	-0.27	31.1	38.3
4-OC_6H_5	-0.03	-0.74	32.3	39.8
4-CH_3	-0.17	-0.14	31.6	40.6
4-OCH_3	-0.27	-0.50	30.5	40.3
3,5-diBr	0.78	-0.36	31.4	40.5
3-NO_2	0.71	0.16	32.0	41.0
3-Br	0.39	-0.18	32.0	40.5
3-Cl	0.37	-0.16	32.0	40.6
3-I	0.35	-0.20	31.8	40.6
3-F	0.34	-0.34	32.0	40.8
3-OCH_3	0.12	-0.50	31.7	40.6
3-CH_3	-0.07	-0.14	31.8	40.8
3,4-diCH_3	-0.24	-0.28	31.8	40.6
3-Cl,4-CH_3	0.20	-0.30	31.6	40.5

Table 59. Electronic spectra of bis(benzoylacetanilido) copper (II) (kK)

Solvent	$\pi_3 \rightarrow \pi_4^*$	$\sigma_L \rightarrow 3d_{xy}$
diethyl ether	30.5	40.3
methanol	30.7	40.8
ethanol	30.6	40.5
1-propanol	30.6	40.5
chloroform	30.4	40.3

Table 60. Electronic spectra of bis(benzoylacetanilido) copper (II) (kK)

Solvent	$d \rightarrow d$
benzene	16.1
chloroform	15.9
acetone	15.8
ethanol	15.5
methanol	15.3
pyridine	14.5

Table 61 Electronic spectrum of N-salicylideneanthranilic acid (in methanol solution)

	Transition Energy (kK)		
N-salicylideneanthranilic acid	24.1	30.3	39.2

Table 62. Electronic spectra of the cobalt N-salicylideneanthranilate complexes Co(R-salanth) (400 - 2200 nm)

R	Transition $^4T_{1g}(F) \leftarrow {}^4A_2$ ‡	Energy	(kK)	
H	~6	11.6	14.7	18.4
5-NO_2	~6	10.6	13.7	18.0
5-Cl	~6	11.4	14.1	18.0
5-CH_3	~6	11.6	14.5	18.0
3,5-diCl*	6.7	10.2		
3,5-diBr†	5.5	11.0		

* sesquihydrate

† hemihydrate

‡ band very broad

Table 63. Electronic spectra of the nickel N-salicylideneanthranilate complexes Ni (R-salanth).H_2O (400 - 1600 nm)

R		Transition	Energy	kK
	*	$^3T_{2g} \leftarrow {}^3A_{2g}$	$^1Eg \leftarrow {}^3A_{2g}$	$^3T_{1g} \leftarrow {}^3A_{2g}$
H	~8	10.6		16.0
5-Cl	~8	10.8	13.4	16.4
5-CH_3	~8	10.4		16.1
3,5-diCl	~8	10.0		16.0
3,5-diBr	~8	10.0		15.9

* shoulder

Table 64. Electronic spectra of the N-salicylideneanthranilate complexes M(salanth)

M	Solvent	Transition Energy (kK)			
Co	methanol	25.5		34.4	41.0
Co	pyridine	*	29.9		
Ni	methanol	24.3		33.3	41.0
Ni	pyridine	23.8	30.4		
Cu	methanol	24.2		35.3	41.0

* Shoulder. Precise frequency unable to be determined.

Table 65. Electronic spectra of the nickel benzoylsalicylidene-hydrazone complexes Ni (BR-SH)$_2$

R		$^3T_{2g} \leftarrow {}^3A_{2g}$	$^3T_{1g} \leftarrow {}^3A_{2g}$	$^3T_{1g}(P) \leftarrow {}^3A_{2g}$
H	~8	11.2	17.5	23.3
3-OCH_3	~8	11.0	17.6	23.3
5-CH_3	~8	10.7	~17	23.2
5-Cl	~8	10.9	17.5	23.4
3,5-diCl	~8	10.3	16.5	23.5
3,5-diBr	~8	10.2	~17	22.8
3,5-diI	~8	10.3	~17	22.3

Table 66. Electronic spectra of the cobalt benzoylsalicylidene-hydrazone complexes Co(BR-SH)$_2$

	$^4T_{2g} \leftarrow {}^4T_{1g}$	$^4T_{1g}(P) \leftarrow {}^4T_{1g}$
H	9.5	23.2
5-CH_3	8.9	22.9
5-Cl	9.5	23.0
3,5-diCl	8.5	22.3

4. MAGNETIC MEASUREMENTS

Table 67. Magnetic moments of the copper benzoylacetanilide complexes $Cu(BzAcR\text{-}An)_2$

R	Magnetic moment (Bohr magnetons)
H	1.82
4-NO_2	1.83
4-OCH_3	1.83
3-Br	1.76
3-Cl	1.81
3-CH_3 (methanol adduct)	1.73
3-Cl (methanol adduct)	1.81

Table 68. Magnetic moments of the N-salicylideneanthranilate complexes M(R-salanth)

M	R	Magnetic moment (Bohr magnetons)
Co	H	4.41
Co	5-NO_2	4.30
Co	5-Cl	4.41
Co	5-CH_3	4.41
Co	3,5-diCl	4.59
Co	3,5-diBr	4.53
Ni	H	3.41
Ni	5-Cl	3.30
Ni	5-CH_3	3.45
Ni	3,5-diCl	3.42
Ni	3,5-diBr	3.28
Cu	H	1.86
Cu	5-NO_2	1.79
Cu	5-Cl	1.82
Cu	5-CH_3	1.82
Cu	3,5-diCl	1.79
Cu	3,5-diBr	1.58

Table 69. Magnetic moments of the metal benzoylsalicylidene-hydrazone complexes $M(BR\text{-}SH)_2$

M	R	Magnetic moment (Bohr magnetons)
Co	H	3.74
Co	5-CH_3	3.89
Co	5-Cl	5.75
Co	3,5-diCl	5.00
Ni	H	2.80
Ni	3-OCH_3	3.18
Ni	5-CH_3	3.15
Ni	5-Cl	3.08
Ni	3,5-diCl	3.08
Ni	3,5-diBr	3.01
Ni	3,5-diI	3.02

Table 70. Magnetic measurements on the copper benzoylsalidylidene-hydrazone ammine complexes $Cu(BR\text{-}SH)(NH_3)(H_2O)$

R	Magnetic moment (Bohr magnetons)
H	1.81
3-OCH_3	1.85
5-Cl§	1.79
3,5-diCl	1.68
3,5-diI	1.72

§ $Cu(BR\text{-}SH)(NH_3)_{\frac{3}{4}}(H_2O)_{\frac{1}{2}}$

Table 71. Magnetic measurements on the copper benzoylsalicylidene-hydrazone α-diimine complexes Cu(BR-SH)(N-N)

R	(N-N)	Magnetic moment (Bohr magnetons)
H	2,2'-bipyridine	1.73
H	1,10-phenanthroline	1.79

Table 72. Magnetic measurements on the copper benzoylsalicylidene-hydrazone complexes $Cu_2(BR\text{-}SH)_2$

R	Magnetic moment (Bohr magnetons)
H	1.03
3-OCH_3	1.70
5-Cl	1.05
3,5-diCl	1.62
3,5-diBr	1.57
3,5-diI	1.58

Table 73 Magnetic moments of metal formazan complexes M(1-Rphenyl,3,5-diphenylformazan)$_2$

M	R	Magnetic moment (Bohr magnetons)
Co	H	1.98 and 2.24 (independent samples)
Co	4-F	1.95
Co	4-Br	1.97
Ni	H	Diamagnetic
Ni	4-NO_2	Diamagnetic
Ni	4-CN	Diamagnetic
Ni	4-Cl	Diamagnetic
Ni	4-I	Diamagnetic
Ni	4-F	Diamagnetic
Ni	4-OCH_3	Diamagnetic
Cu	H	1.77

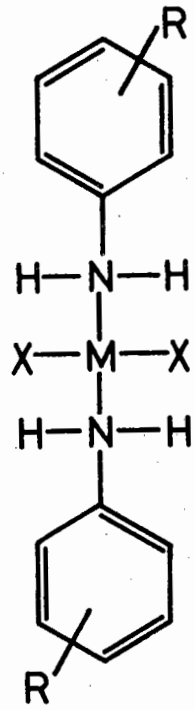
IV. DISCUSSION

1. METAL HALIDE ANILINE COMPLEXES : THE EFFECTS OF ^{15}N-LABELLING AND METAL ION SUBSTITUTION ON THEIR INFRARED SPECTRA.

In this section the infrared spectra of divalent metal dichloro bis(4-methylaniline) complexes (I) are reported. The infrared spectra were determined with the aim of applying ^{15}N-labelling and metal ion substitution effects to the assignment of vibrational frequencies. The infrared spectra of ^{15}N-labelled 4-methylaniline and its metal complexes have not previously been reported.

The complexes of Co(II), Ni(II), Cu(II) and Zn(II) are not isostructural and their structures are of vital importance in the discussion of the effects of metal ion substitution. The Co and Zn complexes have been shown by X-ray crystallographic studies[87-89] to have a tetrahedral arrangement of ligands around the metal ion. Electronic spectral[68,69] and magnetic[84,85] evidence indicates that the Ni complexes have an octahedral arrangement of ligands around the metal ion, presumably having a polymeric structure. The Cu complexes will very probably have the same structure as the similar $CuCl_2(pyridine)_2$ complex[93] with a square planar trans arrangement of ligands around the metal ion and longer Cu-Cl bonds being formed perpendicular to this plane between adjacent molecules.

The ^{15}N-induced shifts of 4-methylaniline and the $MCl_2(4\text{-}CH_3an)_2$ complexes are given in Tables 20 and 21 and are shown in Figures 1 and 2.



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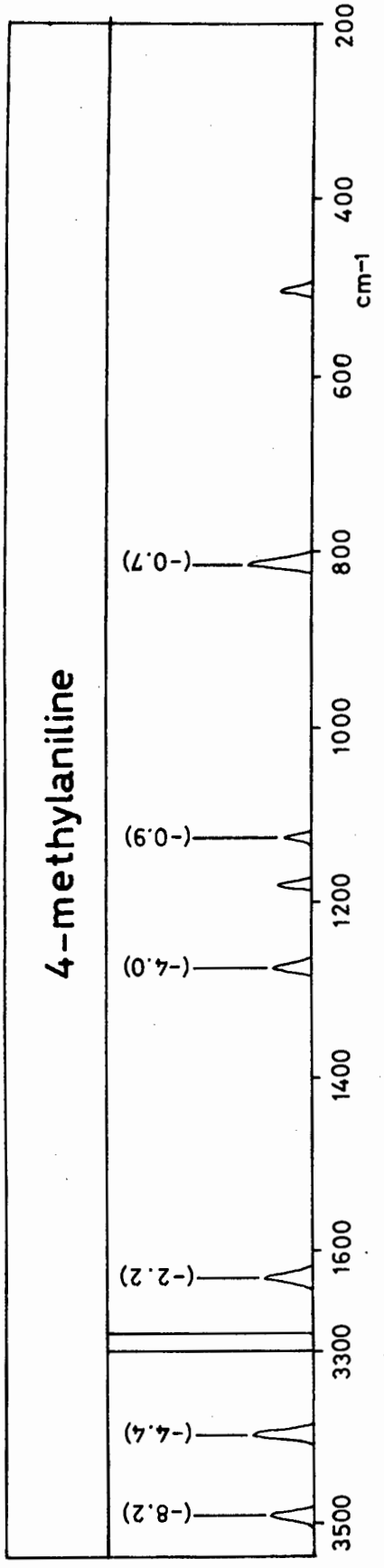


Figure 1. The infrared spectrum of 4-methylaniline.
Figures in parentheses are shifts (cm^{-1}) induced by ^{15}N-labelling.

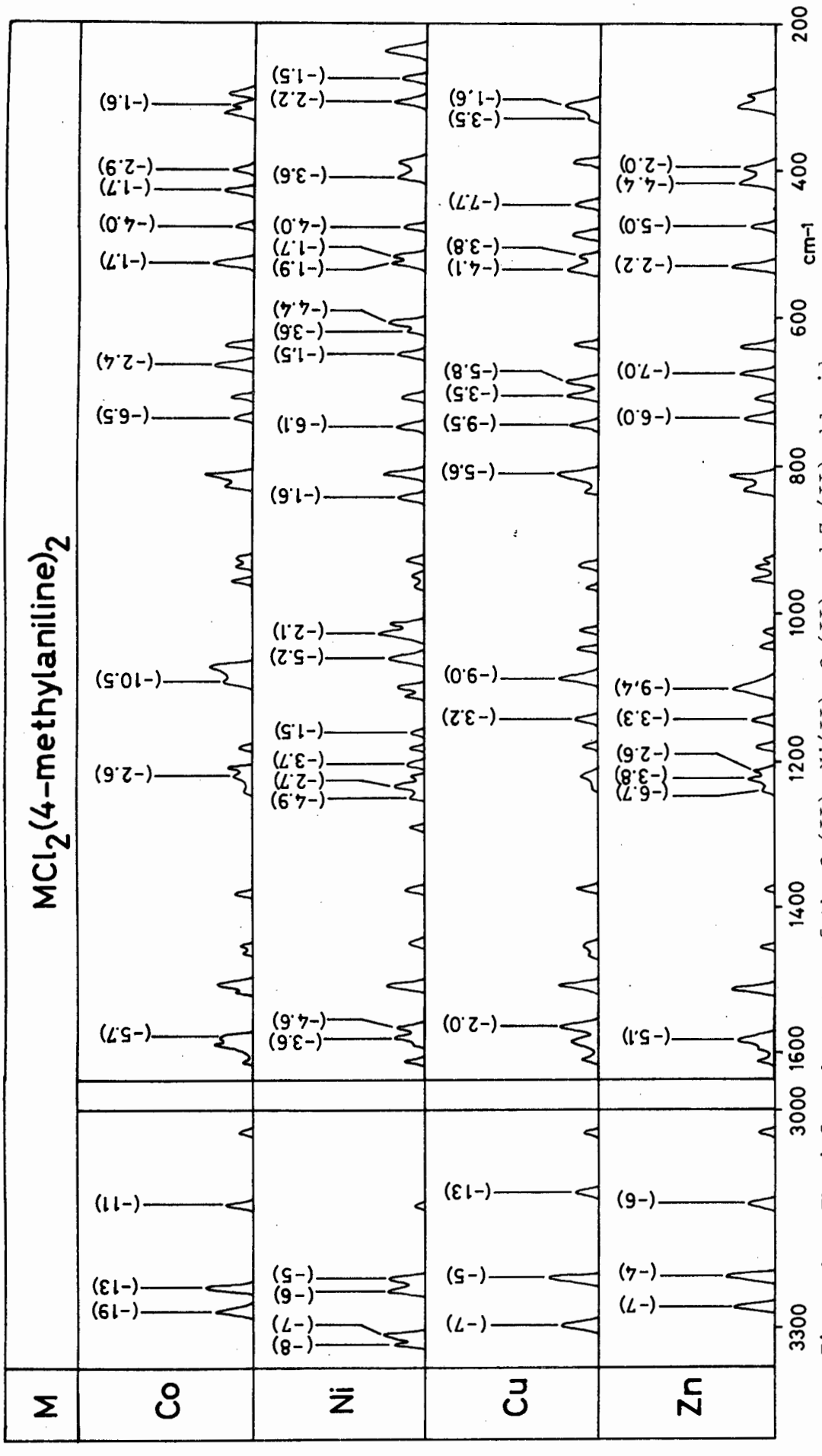


Figure 2. The infrared spectra of the Co(II), Ni(II), Cu(II) and Zn(II) chloride 4-methylaniline complexes.

Figures in parentheses are shifts (cm^{-1}) induced by ^{15}N-labelling. For all other bands the shifts are <1.5 cm^{-1}.

The bands showing ^{15}N-sensitivity in 4-methylaniline correspond very closely with those reported in a similar study on aniline[99]. The bands near 3500 cm^{-1} are assigned to the N-H stretching vibrations and that near 1600 cm^{-1} to the N-H bending vibration. The spectra of both compounds exhibit a band near 1275 cm^{-1} with considerable ^{15}N-sensitivity. This band is reasonably assigned to the νC-N vibration.

The vibrations involving the NH_2 group as an entity, namely the NH_2 twisting, rocking and wagging vibrations, have not been assigned with certainty. In the present study no bands present in the spectra of dilute solutions below that at 1275 cm^{-1} show pronounced shifts on ^{15}N-labelling. Those at 1126 and 812 cm^{-1} show small but statistically significant shifts. These are assigned to the NH_2 twisting and NH_2 wagging vibrations respectively. Tsuboi[99] assigned the ^{15}N-sensitive band at 1115 cm^{-1} to the NH_2 twisting vibration and a broad band in liquid aniline at about 700 cm^{-1} to the NH_2 wagging vibration. These assignments agree with those proposed on the basis of N-deuteration studies of aniline[95,96,98]. The assignment of the band at 812 cm^{-1} is uncertain, as there is also a weak band, the ^{15}N-induced shift of which cannot be determined, near 700 cm^{-1} which could be assigned to the NH_2 wagging vibration and other workers[98,99] report a band near 810 cm^{-1} in aniline which is not however sensitive to ^{15}N-labelling or N-deuteration.

It has been well established[6-17] that in a series of isostructural metal complexes the metal-ligand stretching frequencies parallel the order of the crystal field stabilization energies of the

metal ions. In particular, for octahedral coordination, the frequencies are in the order Co<Ni>Cu>Zn and, for tetrahedral coordination, Co>Ni>Cu>Zn. In the present series of compounds where the structures are not identical the order of frequencies is deranged from either of these sequences. Tetragonal distortion in the case of Cu will cause the frequency to be increased, the bonding power of the metal ion towards the ligands in the plane being increased as the ligands perpendicular to the plane become less strongly bonded. This effect, in the limit with a square planar Cu compound, results in the Irving-Williams stability order[259] of Co<Ni<Cu>Zn. The transition from an octahedral Co compound to the analogous tetrahedral compound will result in an increase of bond strength and vibrational frequency because of the distribution of the bonding power of the metal ion over four bonds instead of six. That this effect will place the vibrational frequency of the Co compound higher than that of the octahedral Ni compound can be seen from the consideration that the frequencies of tetrahedral Co and Ni are in the order Co>Ni and that the frequency of the Ni compound will be further lowered on changing coordination number from four to six. Thus for the series of compounds discussed in this section the order of metal-ligand stretching frequencies will be in the order Co>Ni<Cu>Zn.

Assignment of bands to νM-N will depend on their satisfying two criteria : pronounced ^{15}N-sensitivity and a metal dependence in the order Co>Ni<Cu>Zn. There are two series of bands which satisfy these criteria, occurring within the ranges 400-450 cm^{-1} and 640-700 cm^{-1} (Figure 3). It would be unreasonable to assign the

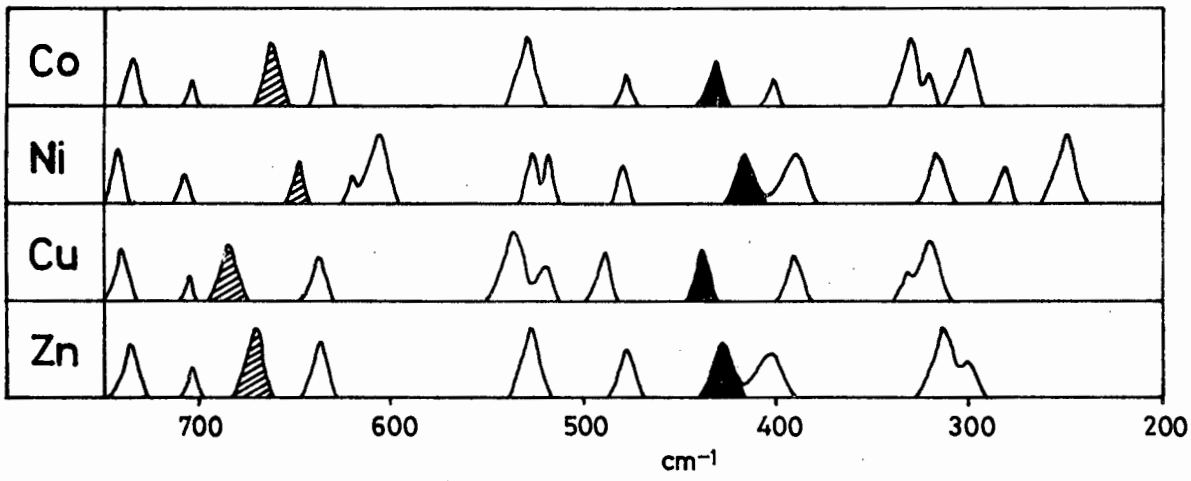


Figure 3. Effect of metal ion substitution on the infrared spectra of metal(II) chloride 4-methylaniline complexes, 200 - 750 cm^{-1}. Solid peaks : νM-N; shaded peaks : NH_2 rocking vibration.

higher frequency band to an uncoupled νM-N vibration since all available data indicate[260,261,262] that νM-N in metal amine complexes does not exceed 600 cm^{-1}. This band is more likely to originate in the NH_2 rocking vibration which has generally been assigned in the range 600-700 cm^{-1} and which is known to exhibit a marked shift on changing the metal ion[5,263].

The band within the range 400-450 cm^{-1} is therefore assigned as the principal or least-coupled νM-N on the basis of its ^{15}N-sensitivity and metal dependence in the order Co>Ni<Cu>Zn. Its position is consistent with previous empirical assignments of νM-N in metal amine complexes[5,67-69,260-263]. Other bands, notably those in the range 475-490 cm^{-1} and 515-535 cm^{-1}, show ^{15}N-sensitivity but their metal dependence is neither large nor precisely in the proposed order. These bands can be assigned to more highly coupled νM-N. Bands between 345 and 390 cm^{-1}, previously assigned as M-N vibrations[68,69,76], exhibit no ^{15}N-sensitivity.

The bands near 300 cm^{-1} have previously been assigned[68,69,75] to νM-Cl. The frequency of the most intense band in this region shows a metal dependence in the order Co>Ni<Cu>Zn which would support its metal-ligand nature. That the vibration is slightly coupled with a vibration involving the nitrogen atom is suggested by its observed ^{15}N-sensitivity.

The bands between 3200 and 3400 cm^{-1} and 1570 and 1590 cm^{-1} are assigned to the νN-H and δN-H vibrations, respectively, the frequencies being lowered from those in the ligand on coordination. These bands are split in the Ni complex, most probably as a result of

the amino groups being in different environments owing to the unique octahedral structure of this complex. The bands near 3100 cm^{-1} are assigned to the N-H stretching vibration where the hydrogen atom is hydrogen bonded, most probably to a chlorine atom. A number of ^{15}N-sensitive bands, which appear between 20 and 50 cm^{-1} below the frequency of the band assigned to νC-N in the ligand, are assigned to this vibration in the complexes. This region corresponds with that of the νC-N absorption previously reported in empirical[68,69] and ^{15}N-labelling[37] studies of primary aromatic amine complexes.

Two series of bands near 1080 cm^{-1} and 740 cm^{-1} show pronounced ^{15}N-sensitivity. Their positions and proximity to the bands so assigned in the ligands, suggest that they be assigned to the NH_2 twisting and NH_2 wagging vibrations respectively.

It has previously been reported that the frequencies of νM-N are in the order Co>Ni>Cu<Zn[76] and that there is an inverse relationship between the frequencies of νM-N and νN-H[76,77,79,81]. The first supposition has been shown above to be incorrect and that the frequency of νM-N for the Cu complex lies higher than that of the other three metal ions. The second supposition also does not hold, either with the stated order of frequencies or with those reported in this work for νM-N. The order of the antisymmetric νN-H is Co<Ni>Cu>Zn, and that of the symmetric νN-H is Co = Ni>Cu>Zn, where however the difference in frequency between the highest and the lowest is only 5 cm^{-1}. The νN-H of which the hydrogen atom is hydrogen bonded, and δN-H have an order of frequencies of Co<Ni<Cu>Zn, which is the Irving-Williams stability order[259]. The

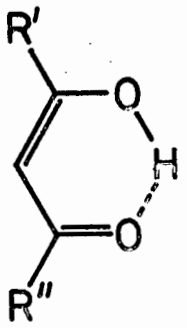
reported order of frequencies of νM-N is the reverse of the Irving-Williams stability order. Selection of another (higher) band in the spectrum of the Cu complex will convert this order into the one reported in the present work. This may account for the incorrect supposition.

2. COPPER β-KETOENOLATE COMPLEXES : THE EFFECT OF LIGAND SUBSTITUTION ON INTRALIGAND AND CHARGE TRANSFER TRANSITIONS IN THEIR ELECTRONIC SPECTRA.

The ultraviolet electronic spectra of transition metal β-ketoenolate complexes have been widely studied[100]. While there is general agreement on the assignment of transitions in the β-ketoenolates of most metal ions, there is some lack of agreement in the case of Cu(II) complexes, particularly in respect of a band near 40kK. In this section, the effect of ligand substitution on the electronic spectra of β-ketoenolates (II), their sodium salts (III) and their copper complexes (IV) is discussed with a view to assigning more conclusively the transitions in the ultraviolet electronic spectra of the copper complexes. The data for compounds studied are given in Tables 52 to 54 and the spectra are shown in Figures 5 to 7 .

The transition energies given by Hückel semi-empirical MO calculations[101-106] and self-consistent field calculations[264] for the intraligand and charge transfer transitions in the acetylacetonate anion and Cu β-ketoenolate complexes are given in Table 74 . The placement of energy levels given by calculation is shown in Figure 4.

The calculations for the acetylacetonate anion, AA^-, and the copper complex, $Cu(AA)_2$, with no, or only limited, π-bonding predict[101,103,106] $\pi \rightarrow \pi^*$ transitions near 33 and 50 kK. A later calculation on a generalized copper β-ketoenolate complex (bis(diformylmethanato) copper(II)) predicts[104,105] $\pi \rightarrow \pi^*$ transitions near 33 and 63 kK, a charge transfer $\sigma_L \rightarrow 3d_{xy}$ transition near 42 kK and a charge transfer $3d \rightarrow \pi^*$ transition near 50 kK. Allowance for



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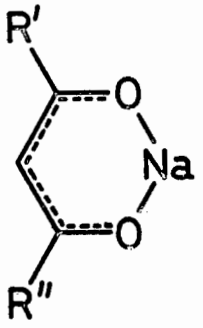

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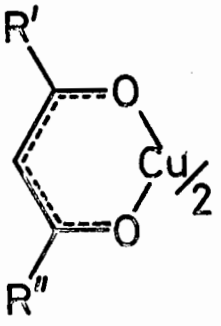


(IV)

Table 74. Calculated transitions in the ultraviolet electronic spectra of β-ketoenolate ions and copper β-ketoenolate complexes.

Species	$\pi_3 \rightarrow \pi_4^*$	$\pi_3 \rightarrow \pi_5^*$	$\sigma_L \rightarrow 3d_{xy}$ (kK)	Reference
AA^-	33.4	49.6		101
AA^- (Hückel)	32.4	47.9		264
AA^- (Self-consistent field)	33.4	53.5		264
$Cu(AA)_2$ (no π-bonding)	32.5	47.8		103
$Cu(AA)_2$ (limited π-bonding)	32.5,34.9	47.8,50.0		103
$Cu(AA)_2$ (pronounced π-bonding)	44.0,47.5	52.1,63.1		103
$Cu(DFM)_2$	32.4,32.9	60.4,65.2	42.4	104,105
$Cu(AA)_2$	28.4,35.3	47.9		106

π-bonding in the calculations[103] indicates that the π energy levels will be split and the transitions will move to higher energy. For the low level of π-bonding[103] found in $Cu(AA)_2$, one component of the $\pi \rightarrow \pi^*$ transitions is unchanged in energy, the other being moved up to 3kK higher in energy (Table 74).

Within the range 28 to 45 kK the electronic spectra of copper(II) β-ketoenolate complexes generally show two intense bands. One of these, in the range 28 to 37 kK, has been unanimously assigned, by virtue of its similarity in energy to a transition in β-ketoenolate ligands and anions and by theoretical calculations[103-106], to the $\pi_3 \rightarrow \pi_4^*$ transition. The second band, in the range 36 to 45 kK, originally suggested[101] to be one component of the $\pi_3 \rightarrow \pi_4^*$ transition moved to higher energy by π-bonding, was subsequently assigned, on the grounds of its sensitivity to change of α-substituents and lack of sensitivity to change of γ-substituents[103,107] and by theoretical

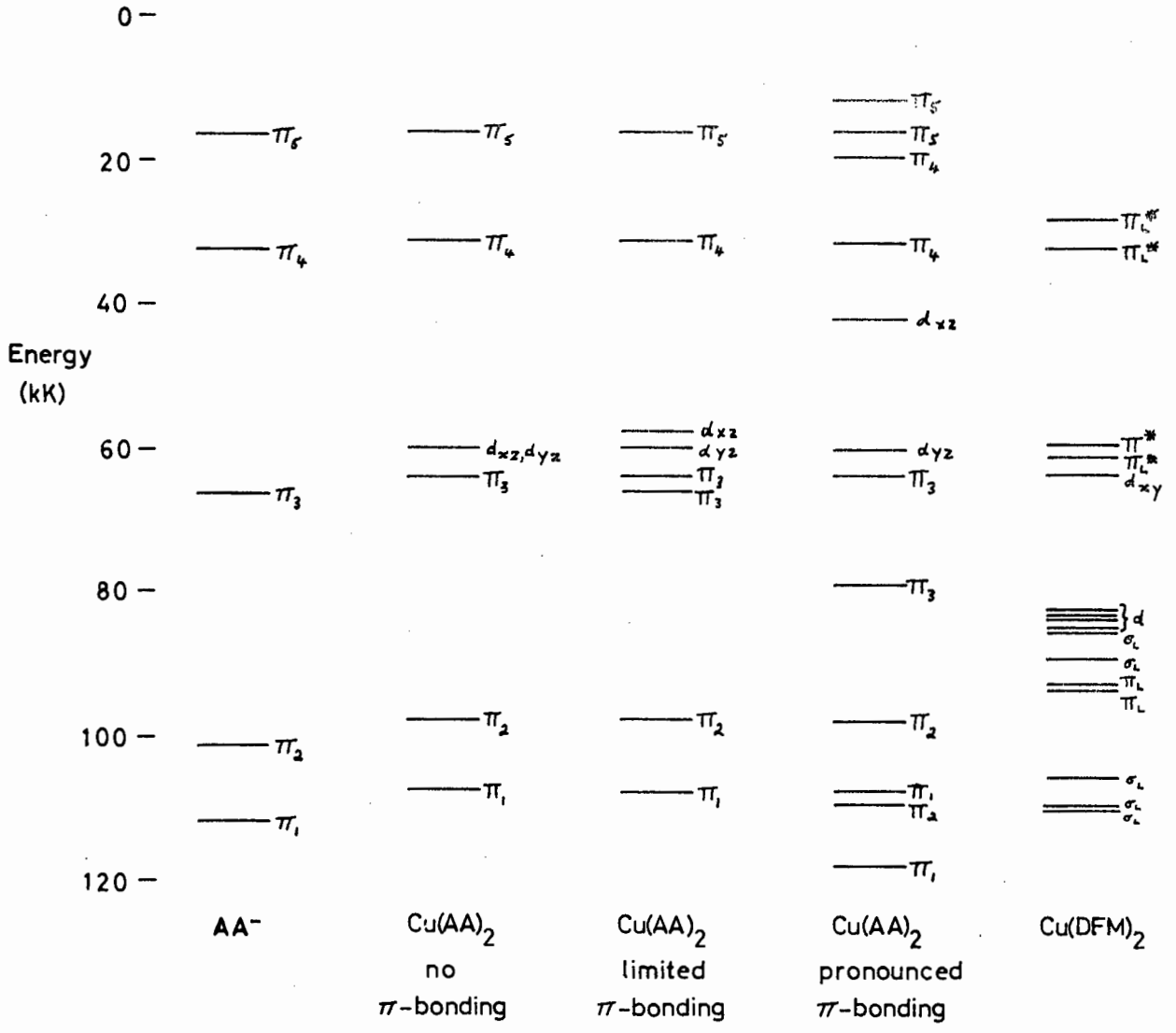


Figure 4. Energy level diagram for the acetylacetone anion and Cu(II) β-ketoenolate complexes.

calculation[104,105] to a charge transfer transition from an oxygen σ-bonding or nonbonding orbital to the copper $3d_{xy}$ orbital.

In work on copper benzoylacetanilide complexes (Section 3) it will be shown that the assignment of the 40 kK band was not unequivocal, owing to the presence in the electronic spectra of the ligands and their sodium salts of bands in the region of 40 kK. A band in this region is generally found in the electronic spectra of β-ketoenolates and their sodium salts when an aryl or heterocyclic ring is present in the molecule (Tables 52 and 53). This transition confuses the question of assigning the 40 kK band in copper β-ketoenolate complexes containing an aryl or heterocyclic ring to the charge transfer transition. In some recent work[108] on copper acetoacetanilide complexes, the earlier assignment of this band to a $\pi \rightarrow \pi^*$ transition was adopted and there is no other record in the literature regarding the assignment of this band in a copper complex where a β-ketoenolate containing an aryl or heterocyclic ring is involved. Comparison of the spectra of β-ketoenolates with or without aryl substituents, their sodium salts and their copper complexes enables the assignment of the charge transfer transition $\sigma_L \rightarrow 3d_{xy}$ to the 40 kK band to be established more convincingly.

Ligands with alkyl substituents.

The spectra of these ligands and their sodium salts exhibit a single intense band between 33 and 42 kK, assigned to the $\pi_3 \rightarrow \pi_4^*$ transition[100]. There is generally a shift to lower energy on formation

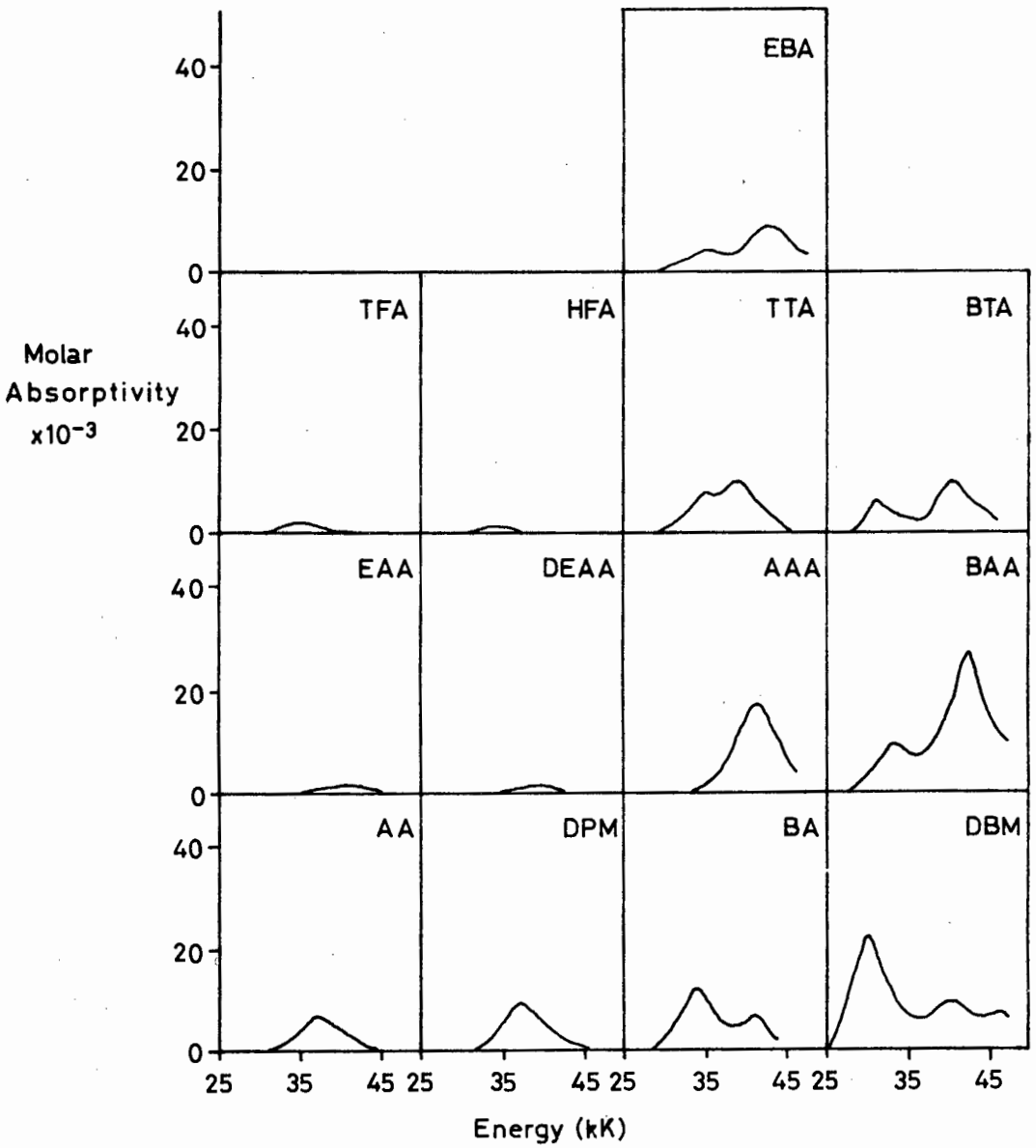


Figure 5. Ultraviolet electronic spectra of β-ketoenolates in methanol solution.

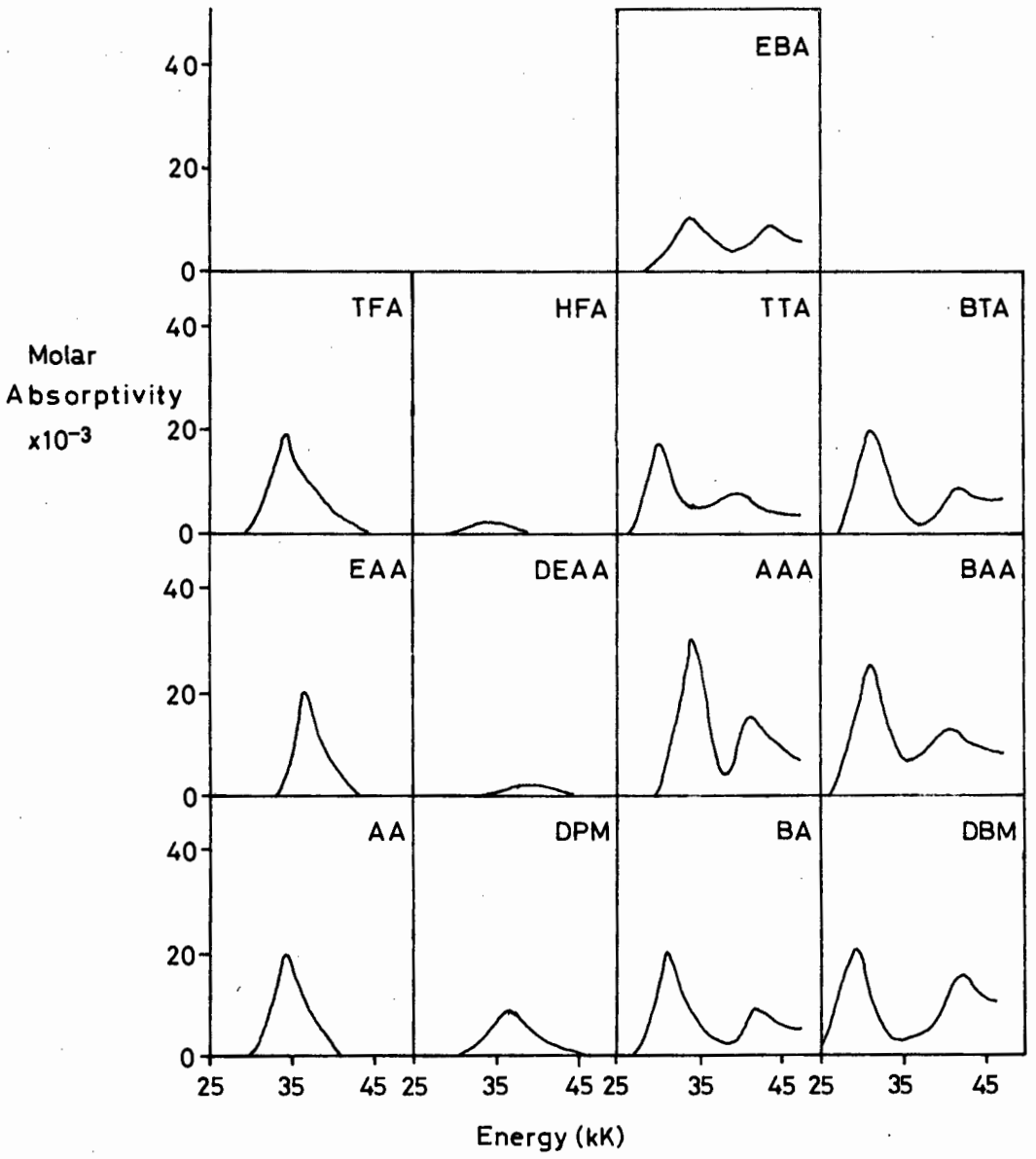


Figure 6. Ultraviolet electronic spectra of the sodium salts of β-ketoenolates in methanol solution.

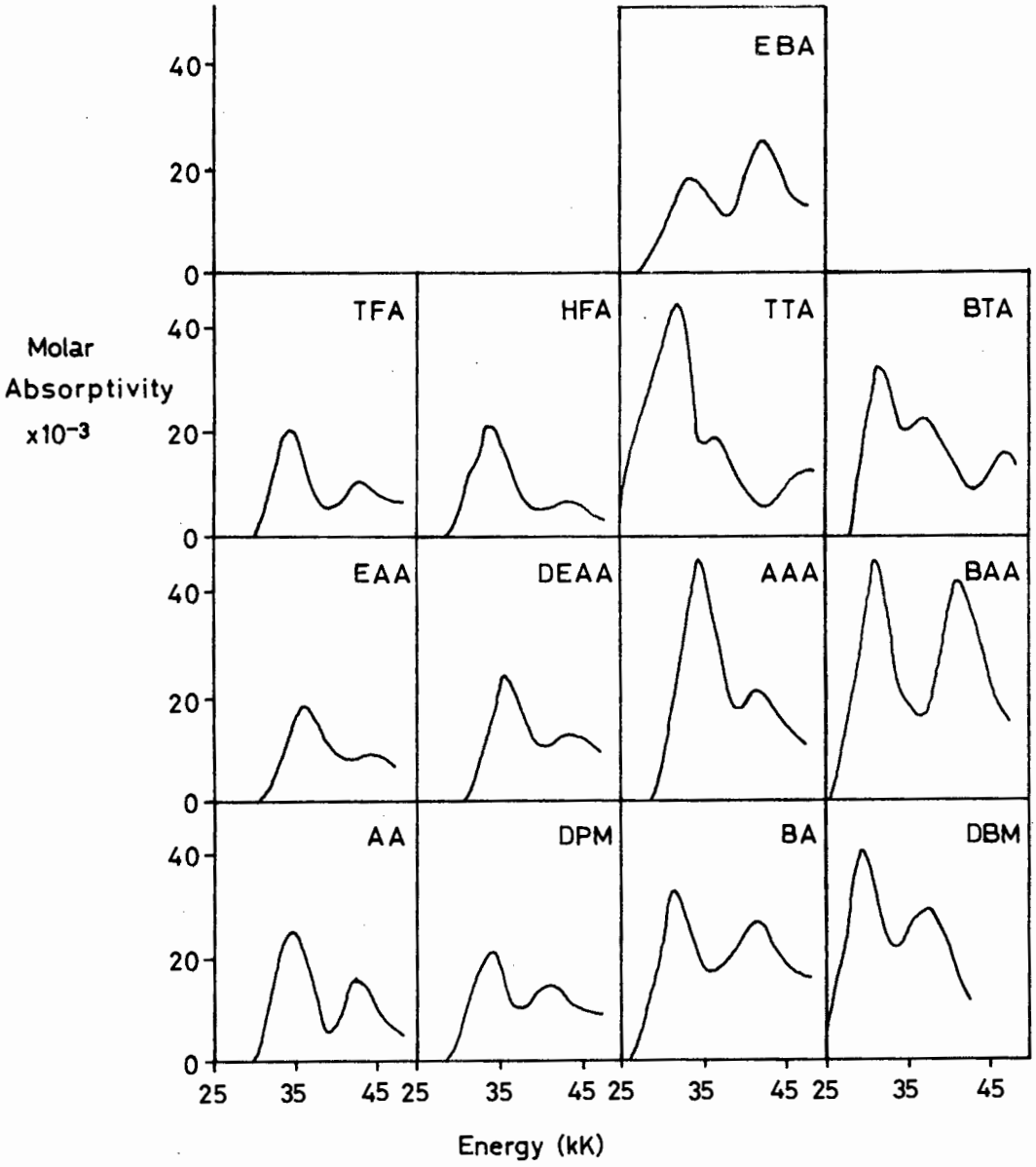


Figure 7. Ultraviolet electronic spectra of Cu(II) β-ketoenolate complexes in methanol solution.

of the β-ketoenolate ion, being a measure of the delocalization energy of the ion relative to the β-ketoenol[101]. It has been considered[265] that in the solid, the alkali metal compounds of β-ketoenolates are covalently bonded with the sodium atom replacing the hydrogen atom of the ligand, rather than existing as ion-pairs. It is probable that in solution, with a large excess of sodium ions present, the same situation prevails. In either case, however, there will presumably be delocalization of electrons within the ketoenolate part of the molecule.

The spectra of the copper complexes of these ligands exhibit two intense bands between 32.5 and 36.5 kK and between 39.5 and 44.5 kK. The lower energy band, which in a number of cases, notably $Cu(AA)_2$ and $Cu(HFA)_2$, shows evidence of having two components, is assigned to the $\pi_3 \rightarrow \pi_4^*$ transition. The absence of marked splitting and the similarity in energy of the bands in the spectra of the copper complexes and the sodium salts of the same β-ketoenolate is evidence that the π-interaction in the complexes is not strong. It is generally accepted on the grounds of ESR[266] and spectroscopic[103,267] evidence that π-bonding in copper β-ketoenolate complexes is small and work on copper benzoylacetanilide complexes (Section 3) has also indicated this. Assignment of the higher energy band to a component of the $\pi_3 \rightarrow \pi_4^*$ transition would necessitate a considerable degree of π-bonding and furthermore the separation in energy of the two components is essentially unchanged, at about 3 kK, over all reasonable strengths of the π-bond.

The higher energy band is also not reasonably assigned to the $\pi_3 \rightarrow \pi_5^*$ transition. Firstly, the observed energy is well below that predicted for the $\pi_3 \rightarrow \pi_5^*$ transition by theoretical calculations (Table 74) which place this transition at least as high as 47.8 kK.

Secondly, the observation that the $\pi_3 \rightarrow \pi_4^*$ transition energies are similar for the sodium salt and the copper complex of each ligand, suggests that this should also be so for the $\pi_3 \rightarrow \pi_5^*$ transition energies whereas no band is observed in the sodium salt spectra in this region. Absence of a second band in the sodium salt spectra favours the assignment of the higher energy band in the copper complexes to a transition other than $a\pi \rightarrow \pi^*$ transition. The remaining reasonable assignment is that predicted by theoretical calculations, namely the charge transfer $\sigma_L \rightarrow 3d_{xy}$ transition. The statement[103] that the energy of this band increases on changing the α-substituents from an electron-releasing to an electron-withdrawing inductive character, is not substantiated in the compounds studied. The transition energy is in the order DPM<AA<HFA<TFA = DEAA<EAA. The $-N(C_2H_5)_2$ group is more electron-releasing than the $-OC_2H_5$ group[110] but both would be expected to be more electron-releasing than the methyl and tertiary butyl groups. It is possible that the $-N(C_2H_5)_2$ and $-OC_2H_5$ groups act anomolously compared to "purely alkyl" groups of that the resonance effect or these substituents outweighs their inductive effect.

The transition energies of the lower energy band increase generally from electron-withdrawing to electron-releasing α-substituents. That this is also generally the order for the ligands and their sodium salts substantiates the assignment in the copper complexes to the $\pi \rightarrow \pi^*$ transition. The order of energies differs for the two bands. The lower energy band has fluoro<alkyl<ester whereas the higher energy band has alkyl<fluoro<ester. The difference in order is

a further argument in assigning the two bands to transitions differing in origin.

Ligands with aryl or heterocyclic substituents.

Whereas the spectra of the alkyl-substituted ligands and their sodium salts exhibit one intense band between 33 and 42 kK, the spectra, when an aryl-substituent is present, shows two intense bands (with the exception of the acetoacetanilide ligand) between 28 and 35 kK and 38 and 44 kK. Acetoacetanilide yields one band hear 41 kK. This difference in behaviour suggests that the additional band originates in a transition associated with the aryl ring. Transitions of monosubstituted benzenes, termed benzenoid or $p\text{-}^1L_a$ transitions, are characteristically found within the range 35 to 45 kK[268]. These bands are usually of lower intensity than the $\pi \rightarrow \pi^*$ bands although the intensities are increased by resonance interaction with the substituents. In the spectra of the sodium salts of these ligands the intensities of the bands near 30 kK and near 40 kK are generally in the approximate ratio 2 : 1. In the ligands themselves the intensities found experimentally will depend on the relative proportion of the keto and enol forms present and the analogous ratio cannot meaningfully be calculated. The energy and relative intensity of the higher energy band suggest that it can be assigned to a benzenoid band, some gain in intensity being acquired through resonance interaction with the β-ketoenolate part of the ion. The lower energy band is assigned, on the grounds of its energy, to the

hybridized, then the anilide and ketoenol rings cannot become coplanar and conjugation between the rings is prevented. It is suggested here that this is the case in acetoacetanilide and the monosodium derivative. The appearance of two bands in the spectra of the sodium salt (which is that of a solution having sodium ions in excess) is typical of a β-ketoenolate having an aryl substituent. It is possible that delocalization of electrons in the ketoenol part of the molecule, whether this be an anion, an ion-pair or an essentially covalently bonded molecule, can attenuate the degree of hybridization of the nitrogen atom, thus allowing conjugation between the anilide ring and the rest of the molecule. The $\pi \rightarrow \pi^*$ transition presumably shifts to a much lower energy because of the increased delocalization over the whole molecule; the band of the benzenoid transition (the intensity presumably enhanced by conjugation and not now obscured by the $\pi \rightarrow \pi^*$ band) now becomes observable.

The spectra of the copper complexes of the aryl-substituted β-ketoenolates exhibit two intense bands between 28.5 and 34.5 kK and between 36.5 and 41.5 kK. The regions of absorption of both bands are generally lower than those of the alkyl-substituted series. The lower energy band is assigned to the $\pi_3 \rightarrow \pi_4^*$ transition for similar reasons to those advanced for the lower energy band in the spectra of the alkyl-substituted β-ketoenolate copper complexes. That the energies and the effect of changing the α-substituents are similar to those of the sodium salts is substantial evidence that the same transition is involved in both cases. The general decrease of transition energy and increase of intensity in the aryl-substituted series is consistent with the expected effects of the increased

electron delocalization produced by conjugation of the aryl ring with the chelate ring. It is perhaps relevant that the acetoacetanilide complex, where a smaller extent of conjugation would be expected, shows the highest transition of this set. The transition energies with varying α-substituents lie in the order DBM<BAA<BTA<BA<TTA<EBA<AAA. This sequence is therefore attributed to the order of decreasing conjugation of the substituent with the chelate ring.

When the band of higher energy is considered it is significant that the ratio between the molar absorptivities of the bands of higher and lower energies is generally considerably greater for the complexes with aryl substituents than for those without aryl substituents (Table 75).

Table 75. Ratio of the molar absorptivities of the higher energy (~40 kK) and lower energy (~33 kK) bands in copper β-ketoenolate complexes.

Ligand abbreviation	$\varepsilon_{40kK}/\varepsilon_{33kK}$
Alkyl substituents	
AA	0.560
DPM	0.692
TFA	0.545
HFA	0.302
EAA	0.516
DEAA	0.578
Aryl or heterocyclic substituents	
BA	0.799
DBM	0.733
AAA	0.429
BAA	0.875
BTA	0.751
TTA	0.404
EBA	1.340

This feature, together with the presence in the spectra of the sodium salts of a band of lower intensity in the same region, strongly suggests

that, in the copper complexes, the higher energy band is derived from the benzenoid and charge transfer $\sigma_L \rightarrow 3d_{xy}$ transitions. In a similar study[269] on β-ketoenolate complexes of oxovanadium(IV) a band was observed in the region near 40 kK only when the β-ketoenolate has an aryl substituent and was assigned as "arising from the primary band in the benzene π system". This observation, which parallels the presence of a similar band in the spectra of the sodium salts, strengthens the argument that in the copper complexes of aryl substituted β-ketoenolates the band in the region of 40 kK has a composite origin. The energy of the higher energy band is in the order TTA<BTA<DBM<BA<BAA = AAA<EBA. The order differs from that of the lower energy band in that the fluoro-substituted β-ketoenolates show the lowest energies but there does not seem to be any logical explanation for the order of substituent dependence.

The results of this study of the copper complexes of thirteen β-ketoenolates with α-substituents having widely differing electronic properties, together with the ligands and their sodium salts, has confirmed the assignment of a band within the range 28 to 36 kK in the copper complexes to the $\pi_3 \rightarrow \pi_4^*$ transition. The band within the range 36 to 42 kK in the copper complexes is assigned, both when an aryl α-substituent is present and when only alkyl α-substituents are present, to the charge transfer $\sigma_L \rightarrow 3d_{xy}$ transition. This assignment has not previously been made in the case where aryl substituents are present and the band must in these cases be considered to be a composite band originating in the charge transfer transition and the benzenoid transition.

Extent of π-interaction in copper(II) β-ketoenolate complexes.

Most of the available evidence from ESR[266] and electronic spectra[101-103] suggests that the extent of π-overlap in the copper-oxygen bonds of copper(II) β-ketoenolate complexes is small and certainly significantly less than that which exists in most octahedral β-ketoenolate complexes of metal(III) ions of the first transition series. In the present work, the observation that the $\pi_3 \rightarrow \pi_4^*$ transition energies of the sodium salts and copper complexes of a particular ligand are of similar magnitude also indicates a low level of π-bonding. The data[269-271] on $\pi_3 \rightarrow \pi_4^*$ transition energies of eight

Table 76. $\pi_3 \rightarrow \pi_4^*$ transition energies of metal β-ketoenolates (kK)

Metal	Ligand Abbreviation					Reference
	DBM	BA	TFA	DPM	AA	
VO(IV) *	27.4	30.3	32.7	33.1	32.6	269
Cu(II) †	28.7	31.3	33.9	33.7	34.3	this work
Na(I) †	28.8	30.9	34.1	36.0	34.1	this work
Al(III)§	28.6	31.3	34.3	34.0	34.8	270, 271
Mn(III)§	29.1	32.4	34.2	36.5	36.8	270, 271
Fe(III)§	30.0	33.2	36.5	36.2	36.8	270, 271
Cr(III)§	31.2	34.2	35.8		37.0	270, 271
Co(III)§	33.6	36.1	38.3		39.1	270, 271

* in acetonitrile

† in methanol except $Cu(DBM)_2$ in chloroform

§ in chloroform

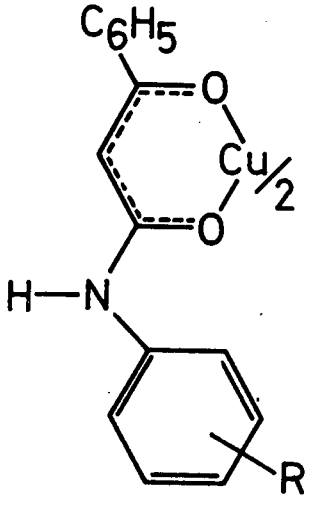
metal ions with five β-ketoenolate ligands (Table 76) places the Cu(II) ion near Al(III) and Na(I) (where metal-ligand π-bonding is

electronically prevented) and VO(IV) (where structural considerations minimise metal-ligand π-bonding).

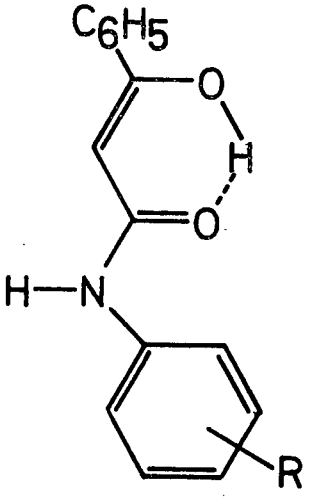
3. BENZOYLACETANILIDE COPPER COMPLEXES: THE EFFECT OF LIGAND SUBSTITUTION ON THEIR STRUCTURE AND INFRARED AND ELECTRONIC SPECTRA.

In this section the infrared and electronic spectra of the Cu(II) complexes (V) of variously substituted benzoylacetanilides, the electronic spectra of the benzoylacetanilide ligands (VI) and their sodium salts (VII) and the infrared spectra of some Cu(II) acetoacetanilide complexes (VIII) are reported. The infrared spectra were determined with the aim of applying substituent effects to the assignment of metal-ligand stretching frequencies. The effect of ligand substitution on the electronic spectra was examined in order to elucidate the nature of the metal-ligand bonding. Infrared and electronic spectra were further used to investigate the structure of methanol adducts of copper complexes of benzoylacetanilides substituted in the 3-position of the anilide ring. Apart from the values reported for the unsubstituted compounds[141,155] and the visible spectra of the unsubstituted and three of the substituted compounds[129], the infrared and electronic spectra of copper complexes of aceto- and benzoyl-acetanilides have not previously been reported.

The magnetic moment of bis(benzoylacetanilido) copper(II) was reported[155] to have the subnormal value of 1.40 Bohr magnetons, whereas the same author reported[129] magnetic moments of copper acetoacetanilide complexes within the normal range for one unpaired electron. In the present study, values of a number of copper benzoylacetanilide complexes are within the normal range (Table 67). Furthermore, in a review[200] of subnormal magnetic moments of Cu(II) complexes, no examples are cited of a β-ketoenolate complex of Cu(II) having a



(V)



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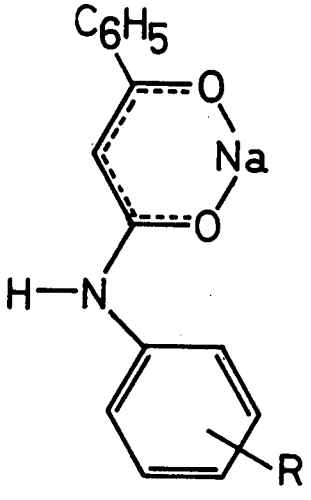

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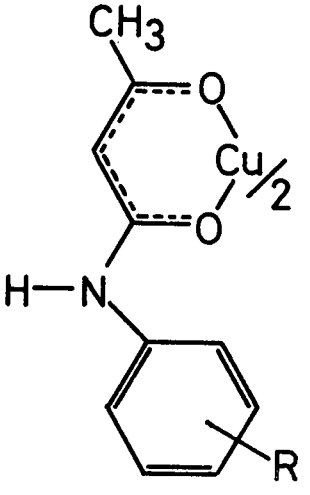
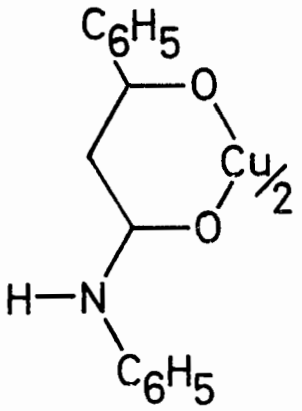
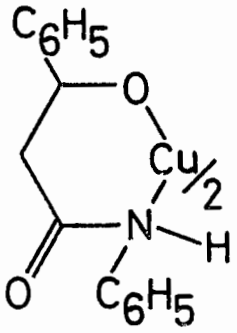


(VIII)

subnormal magnetic moment.

There are three potential bonding sites in the benzoylacetanilide ligands: the two oxygen atoms and the nitrogen atom. Formation of a chelate ring is possible in two ways - by coordination through two oxygen atoms or through the nitrogen and an oxygen atom, giving the alternative structures:





In both cases, the enol proton bound to an oxygen atom is considered to be lost on coordination. Coordination by nitrogen is less likely because of steric considerations and does not fit the experimental facts that a band, corresponding to νN-H, is found in the infrared spectra of the complexes at a higher frequency than the highest of a variable number of bands found in the same region of the spectra of the corresponding ligands. Coordination through the nitrogen atom would be expected to give a lower frequency than that found in the ligands.

Adduct formation.

A striking feature of the benzoylacetanilide complexes is the ability of those with a substituent in the 3-position of the anilide ring to adduct two molecules of methanol per atom of copper with a simultaneous change of colour from green to brown. This results merely on contact of the complexes with cold methanol, the change in colour taking place within a matter of minutes. Contact with any other common solvent reverses the process, the methanol being removed and the complex restored. Adduction of no solvent molecule other than methanol is observed. The behaviour is not observed when a nitro substituent is present in the 3-position, when a bromo substituent is present in the 5- as well as the 3-position or when a substituent is present only in the 4-position. It is also not observed for a number of acetoacetanilide complexes prepared.

The existence of brown and green forms of copper complexes has been reported in a considerable number of compounds. An early example was the report of Pfeiffer and Glaser[272,273] that bis(2-hydroxy-N-methyl-1-naphthaldimine)copper(II) could be obtained in either a green or brown crystalline form. Waters and coworkers have investigated this phenomenon in two series of papers[274-301] in which electronic spectra, crystal structures and conformations of molecules are discussed. Their original proposal[274] was that the brown compounds contain copper atoms which are strictly four-coordinate whereas the green compounds contain either five- or six-coordinate copper. This conclusion was supported by the fact that both forms of a number of compounds yield green solutions in pyridine and other coordinating solvents and brown or violet solutions in non-coordinating solvents

such as carbon tetrachloride. Increase of the coordinating power of the solvent leads to increase of absorption near 700 nm and decrease of absorption near 500 nm. This is consistent with the colour changes observed and it was assumed that they are brought about by solvent coordination to the metal. The same spectral differences are observed for the two forms of the compounds when investigated in potassium bromide discs[275].

A number of subsequent crystal structure determinations[276-278,282,288,290,291] supports this relationship between colour and coordination number of the copper atom. Green N,N'-di-salicylidenepropane-1,2-diaminecopper(II) monohydrate was found to have the donor atoms in a square pyramidal arrangement around the copper atoms[276]. Green N,N'-ethylenebis(salicylaldiminato)copper(II) was found to be dimeric with two long Cu-O bonds between the two halves of the dimer, each copper atom thus becoming five-coordinate[277]. Purple N,N'-ethylenebis(acetylacetoneiminato)copper(II) shows essentially four-coordination with nearest approaches to the copper atom perpendicular to the coordination plane being a carbon atom at 3.38A[278].

It was shown that this explanation of what was termed "colour isomerism" is not rigidly true in that it was reported[301] that bis(salicylaldiminato)copper(II) is green and is isomorphous with the 4-coordinate nickel compound. More definitely, the so-called γ-form of bis(N-methylsalicylaldiminato)copper(II) is brown and consists of dimers with two Cu-O bonds between the halves, the copper atom being five-coordinate[289]. Nevertheless, the colour of a copper complex, when brown and green forms are found, was still

held[278] to be a reasonably reliable indication of the coordination number.

It was also proposed[302], following a study of copper complexes of peptides and similar ligands, that the colour of a copper complex and the coordination number of the copper atom is a function of the ligand field strength of the donor atoms. Weaker ligands are associated with increase of coordination number and a green colour.

This phenomenon is related to the fact that the acetic acid[303], phenol[303] and 4-nitrophenol[297] adducts of N,N'-ethylene-bis(salicylaldiminato)copper(II) are violet or dark red in colour. In the 4-nitrophenol adduct there are no axial approaches to the copper atom and the adduct molecule is bound to the ligand by a hydrogen bond between the phenol group and one of the oxygen donor atoms of the ligand. The parent compound is green and is structurally composed of dimeric five-coordinate molecules[277]. That the adducted molecules are not simply coordinated to the copper atom of the monomeric species is suggested by the colour in that the "water adduct" of the similar compound N,N'-disalicylidenepropane-1:2-diamine copper(II) is green and the structure involves five-coordinate copper atoms with an axial copper-water bond[276]. A further similar example occurs in the case of the N,N'-ethylenebis(acetylacetoneiminato)copper(II) complex where the anhydrous form and the hemihydrate are violet and the monohydrate is green. In the monohydrate the water molecule is coordinated to the copper atom [282,295] whereas in the hemihydrate it is hydrogen bonded to one of the oxygen donor atoms of the ligand[288] and the closest axial approach to the copper atom is at 3.65A. In the

anhydrous form the copper atom is essentially four-coordinate with an approach of 3.38A between the copper atom and one of the carbon atoms of the chelate ring of a neighbouring molecule[278]. Further, in the violet methylammonium perchlorate adduct of N,N'-ethylenebis(acetylacetoneiminato)copper(II)[296] and the dark red chloroform adduct of N,N'-ethylenebis(salicylaldiminato)copper(II)[298], the adduct is hydrogen bonded to donor oxygen atoms.

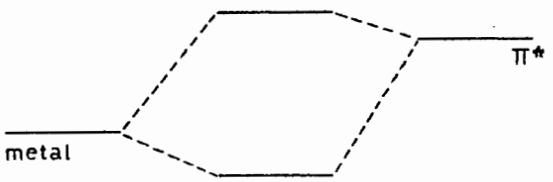
That the ligand field strength can influence the coordination number is seen by comparison of the structures of 1,2-bis[(2-aminobenzylidene)amino]-proponato(2-)copper(II) having four nitrogen donor atoms[299] and N,N'-disalicylidene-1,2-diaminecopper(II), the analogue having two nitrogen and two oxygen donor atoms[276]. The former compound exists as discrete molecules with a four-coordinate copper atom whereas the latter compound embodies a coordinated water moleucle giving square pyramidal coordination around the copper atom. The increase in ligand field strength in changing from a N_2O_2 donor set to an N_4 donor set has led to a consequent decrease in coordination number.

This evidence makes it clear that the ligand field strength can influence the coordination number of the copper atom. Hydrogen bonding of an adduct molecule to the ligand acts to increase the ligand field strength and to consequently decrease the ability of the copper atom to form a fifth bond.

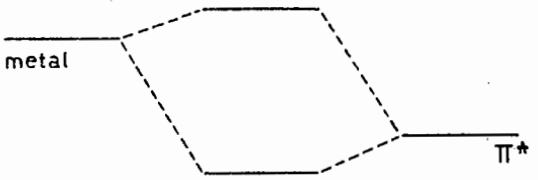
This phenomenon is clearly related to the spectrochemical series and leads to the view that the effect of the π and π^* orbitals of the donor atoms on the orbitals of the copper atom are important

in the determination of the coordination number and the colour of copper complexes.

When an atom of a conjugated system such as an aromatic aldehyde is the acceptor in a hydrogen bond, the energy of the $\pi \rightarrow \pi^*$ transition is reduced[304]. It is presumed that the π^* orbital, being more peripheral than the π orbital, is more accessible for hydrogen bond formation and is thus stabilized relative to the π orbital[305]. In a copper complex, the ligand may possess a π^* orbital which can interact with a metal orbital to form a pair of molecular orbitals. Depending on their relative energies the resulting bonding orbital may be "metal-like" (i) or "π^*-like" (ii).

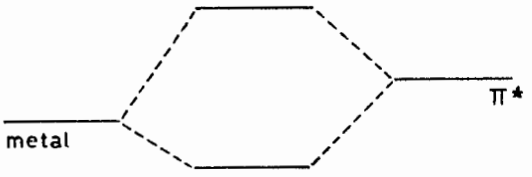


(i)



(ii)

If "metal-like", then a fifth bond to the copper atom may be formed by overlap with the p_z orbital of the oxygen atom of an adjacent molecule or water molecule, lowering the energy of the π^* orbital by hydrogen bonding would then diminish the "metal-like" character of the bonding molecular orbital (iii) and thus reduce the tendency for additional bond formation.



(iii)

In the benzoyl- and aceto-acetanilide copper complexes, production of the adducts is only realised with methanol and the 3-substituted benzoylacetanilide complexes. Adduct formation, however, does not take place with the 3-NO_2 and 3,5-diBr substituents. These substituents are distinguished from the other 3-position substituents in having, by far, the highest electron withdrawing σ_m values. However, the remaining 3-position substituents do not have electronic properties which uniquely distinguish them from the 4-position substituents, whatever substituent parameter is used as a measure of its electronic effect.

A distinction between 3- and 4-position substitution is that the 3-position allows isomers involving two alternative dispositions of the substituent relative to the chelate ring, if free rotation of the anilide ring about the C-N bond is prevented. A degree of electron delocalization could prevent such rotation. Substitution in the 4-position or in both the 3- and 5-positions does not allow such isomers. However, this type of isomerism as a factor in arriving at an explanation of the method adduction is rendered unlikely by the absence of adduction with 3-NO_2 substitution and with the acetoacetanilide complexes.

The methanol solutions of all the complexes, including those with 3-substituents, are green. The wavelength of the maximum of the $d \rightarrow d$ absorption peak is similar to that for other solvents (Table 60). This would indicate that in solution the copper atoms are six-coordinate, with methanol (or other solvent molecules) coordinated to the copper atoms.

In the light of the findings[288,296-298] that adducted molecules can be hydrogen bonded to ligand donor atoms, it is not impossible that, in the solid adducts, methanol molecules are bonded to the ligand donor atoms and not to the copper atoms. This supposition accords with the experimental fact that the methanol molecules are not strongly bound and are spontaneously lost at room temperature in air over a period of a few days and, under vacuum or at moderately elevated temperatures, within a period of a few hours. In terms of the previous suggestion of Waters[278] the brown methanol adducts have four-coordinate copper atoms, whilst in the green complexes a coordination of six is achieved by bonds, perpendicular to the coordination plane, to nitrogen atoms of adjacent molecules. The infrared spectra of the complexes and the adducts are quite definitely different, particularly in the region below 600 cm^{-1} (Figure 8). This indicates a structural difference between the complexes and the adducts.

The arguments presented previously concerning the energy of the π^* orbital of the ligand are possibly relevant to the phenomena found with the benzoylacetanilde complexes. If the methanol molecules are hydrogen bonded to the ligand donor atoms, then the π^* orbital is lowered in energy, making the bonding molecular orbital less "metal-like" and thus reducing the tendency for axial bonding. The rôle of the 3-position substituent may be solely that it is involved in also being hydrogen bonded to the methanol molecule. The effect of the 3-NO_2 and 3,5-diBr substituents in preventing adduction may be related to their electron withdrawing properties, but the present work does not enable this point to be established conclusively.

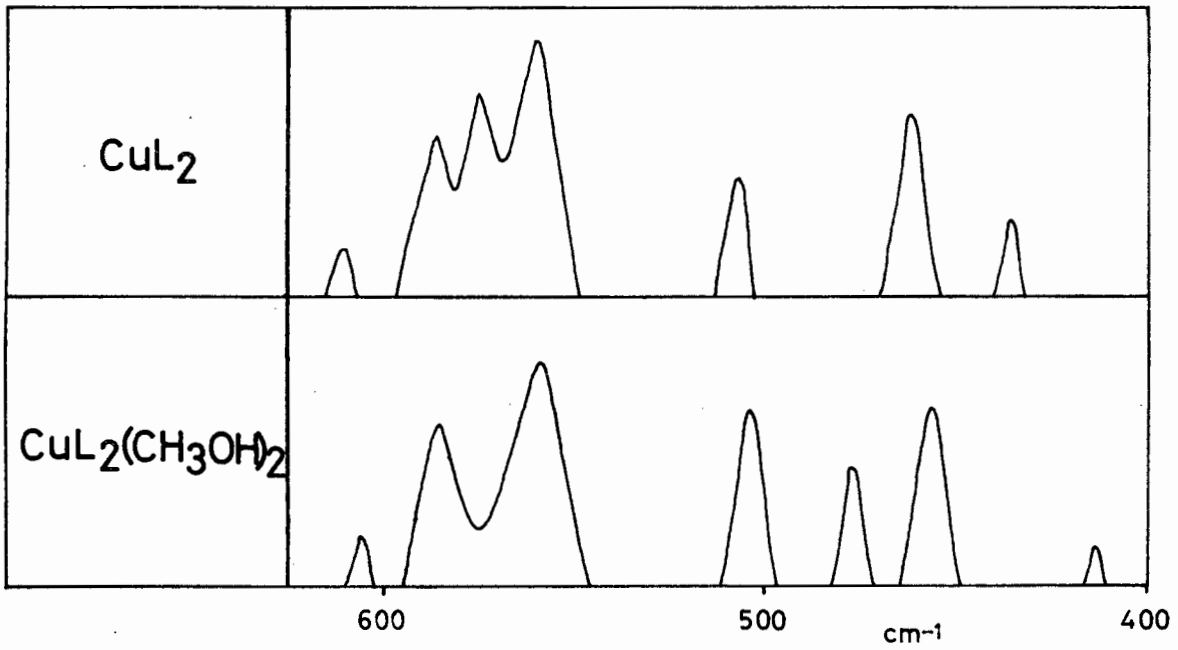


Figure 8. Comparison of the infrared spectra, 400 - 625 cm^{-1}, of $Cu(BzAc3\text{-}OCH_3An)_2$ and $Cu(BzAc3\text{-}OCH_3An)_2(CH_3OH)_2$.

The difference between the benzoylacetanilide and aceto-acetanilide complexes lies only in the replacement of a methyl group by a phenyl group. This would extend the conjugation path, which could result in a lowering of the π^* orbital energy to the critical extent necessary to make further lowering by hydrogen bonding enough to affect the coordination number and hence the colour. It is not clear why methanol molecules should not, however, become hydrogen bonded in the acetoacetanilide complexes. Presumably it is necessary to have a π-orbital of suitable energy before hydrogen bonding takes place. It is perhaps relevant to this argument that the 4-phenyl substituted benzoylacetanilide complex is the only complex which is brown. Methanol adduction, however, does not occur. Possibly the lowering of the π^* orbital energy, by extension of the conjugation path, is also responsible in this case for preventing six-coordination. The infrared spectrum of this complex differs from that of the other 4-substituted complexes and the electronic spectrum is similar to that of the methanol adducts (Figure 13).

The above discussion is intended to point out the experimental facts concerning the methanol adduction in the light of the previous work and theories concerning colour and coordination patterns in copper complexes. The purpose of the investigation into the properties of the benzoylacetanilide complexes was to investigate the copper-oxygen bonding and the effect of ligand substitution on this by using infrared and electronic spectroscopy. A fuller investigation of the question of methanol adduction would certainly involve the synthesis of other ligands and the use of further techniques, particularly X-ray crystallography. It was not considered desirable to extend the investigation in this direction.

Infrared spectra.

The infrared spectra of the complexes are given in Tables 22 to 26 and the region between 200 and 600 cm^{-1} is shown in Figures 9 to 11 .

The N-H stretching vibration, νN-H, occurs as a sharp absorption in the range 3320 - 3430 cm^{-1}. The frequencies are between 30 and 150 cm^{-1} higher than those of the ligands, confirming that coordination occurs through the oxygen atoms and does not involve the nitrogen atom. In the methanol adducts no sharp band occurs in this region, diffuse absorption resulting from overlap of νN-H and νO-H bands and from band broadening due to hydrogen bonding effects.

Table 77 shows that the complexes can be divided into two groups on the basis of the frequency of νN-H.

Table 77. N-H stretching frequency, νN-H, of the complexes $Cu(BzAcR\text{-}An)_2$

R	σ	νN-H	R'	σ	νN-H	
4-F	0.06	3431	$4\text{-}NO_2$	0.78	3356	3248
$3,4\text{-di}CH_3$	-0.24	3430				
$3\text{-}Cl,4\text{-}CH_3$	0.20	3414	$3\text{-}OCH_3$	0.12	3353	*
$4\text{-}NHCOCH_3$	-0.01	3412				
4-Cl	0.23	3411	4-CN	0.63	3333	3236
$4\text{-}CH_3$	-0.17	3410	$4\text{-}COCH_3$	0.52	3322	*
3-Cl	0.37	3409	$4\text{-}OCH_3$	-0.27	3328	3244
3-Br	0.39	3407				
3,5-diBr	0.78	3406				
$3\text{-}NO_2$	0.71	3406				
$3\text{-}CH_3$	-0.07	3406				
H	0.00	3402				
3-F	0.34	3402				
4-Br	0.23	3400				
$4\text{-}OC_6H_5$	-0.03	3399				
3-I	0.35	3397				
4-I	0.28	3389				

* Precise frequency not able to be determined owing to weak intensity.

The one group has values between 3389 and 3431 cm^{-1} whilst the other group has values between 3328 and 3356 cm^{-1} with a second, less intense, peak at a frequency about 100 cm^{-1} lower. A common feature of the substituents in the second group is they contain an oxygen or nitrogen atom and thus could be involved in hydrogen bonding with the anilide hydrogen atom, νN-H being consequently decreased. There is no correlation of νN-H with the Hammett σ value nor with Swain and Lupton's[27] *F* and *R* parameters. It can be seen, however, that for 4-substituted halogens, the frequencies increase in the order of the electronegativities of the halogen atoms. Furthermore, the range of values is greater for the 4-substituted halogens (42 cm^{-1}) than the 3-substituted halogens (12 cm^{-1}).

In the spectra of metal acetylacetonates, two bands occur near 1590 and 1520 cm^{-1} which are characteristic of the chelate ring in which both carbon-oxygen bonds are fully equivalent[306]. In the benzoylacetanilides the situation is complicated by the presence in the molecule of both phenyl and anilide rings. Generally the spectra of all the complexes show four bands between 1530 and 1630 cm^{-1}. These are a broad, intense band near 1540 cm^{-1}, two bands between 1570 and 1610 cm^{-1} and a band which is generally observed above 1620 cm^{-1}. If the benzoylacetanilide complexes are considered as analogous to other β-ketoenolate complexes, then the bands near 1540 and 1590 cm^{-1} may be assigned to νC ═ O.

In previous studies[307] on the infrared spectra of metal β-ketoenolates, bands in the range 400 - 650 cm^{-1} have been assigned to the principal νM-O. ^{18}O-Labelling studies[53] of metal acetylacetonates have led to the assignment of two bands within this range to νM-O, the

band of higher frequency being the vibrationally purer (less coupled) metal-oxygen stretching band. It has been shown[308] that the principal νM-O bands of metal β-ketoenolates are highly sensitive to the electronic effects of the chelate ring substituents. Thus successive replacement of the methyl groups of acetylacetone by phenyl groups causes the frequency separation between the two bands to decrease while substitution of electron withdrawing groups by electron releasing groups shifts νM-O towards higher frequency. Substitution on a phenyl ring has been found to shift metal-ligand stretching frequencies in metal salicylaldehyde[308], N-arylsalicylaldimine[15,16] and anthranilate[12] complexes. The shifts have been explained in terms of electronic effects of the substituents.

In the infrared spectra of the Cu(II) benzoylacetanilide complexes, a shift of νCu-O would be expected to be induced by electron releasing substituents, since these substituents will increase the donor capacity of the oxygen atoms for the Cu(II) ion and hence serve to increase the copper-oxygen force constants. A pair of bands, for most of the complexes, and a single band, for the adducts, (Figures 9 to 11 and Table 78) within the reported νCu-O range are observed to shift towards higher frequency in the order of the electron releasing capacity of the substituents as determined by their Hammett parameters, σ_m and σ_p. These bands are therefore assigned as the principal νCu-O bands.

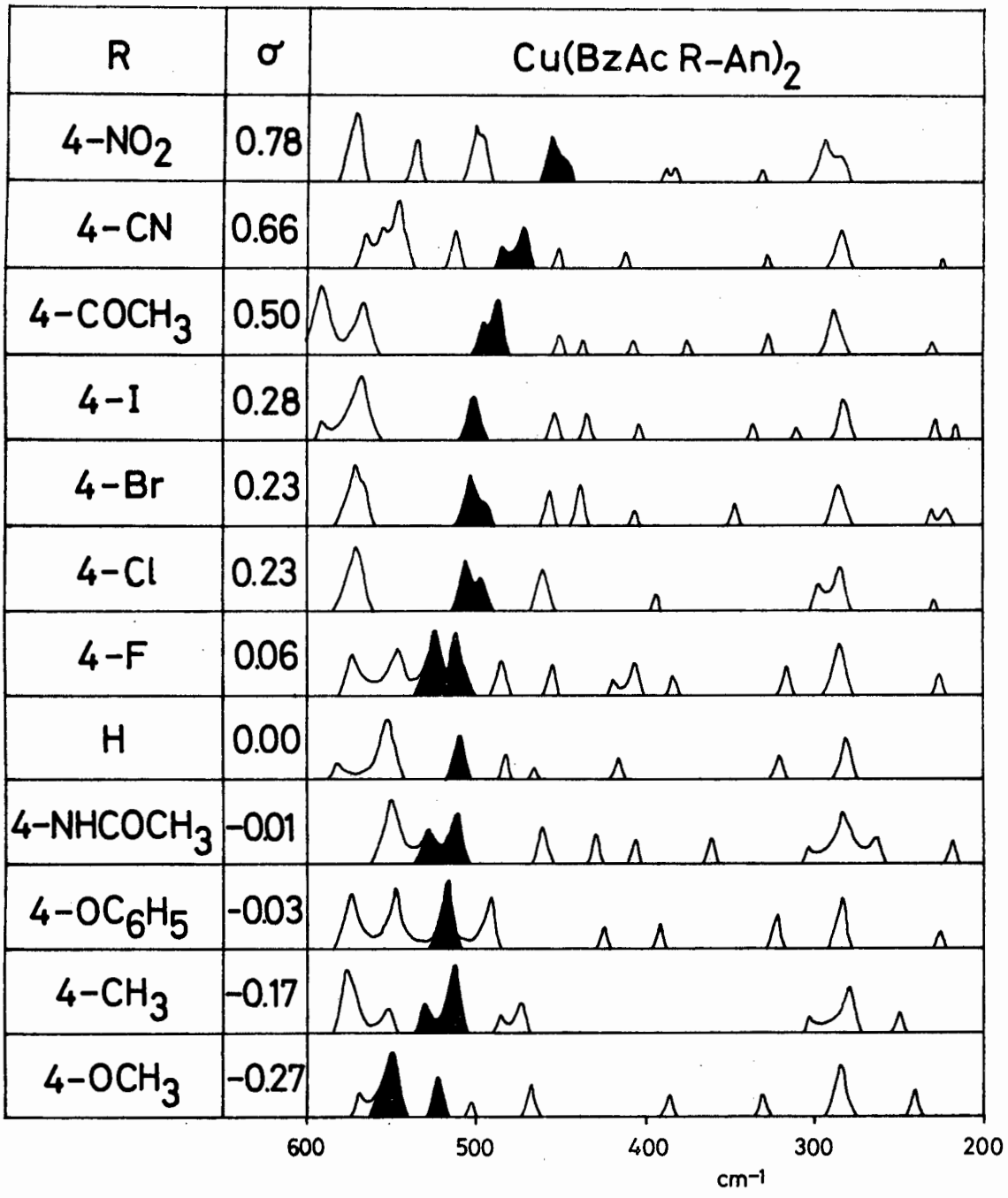


Figure 9. The infrared spectra of 4-substituted Cu(II) benzoylacetanilide complexes, 200 - 600 cm^{-1}. Solid peaks : νCu-O.

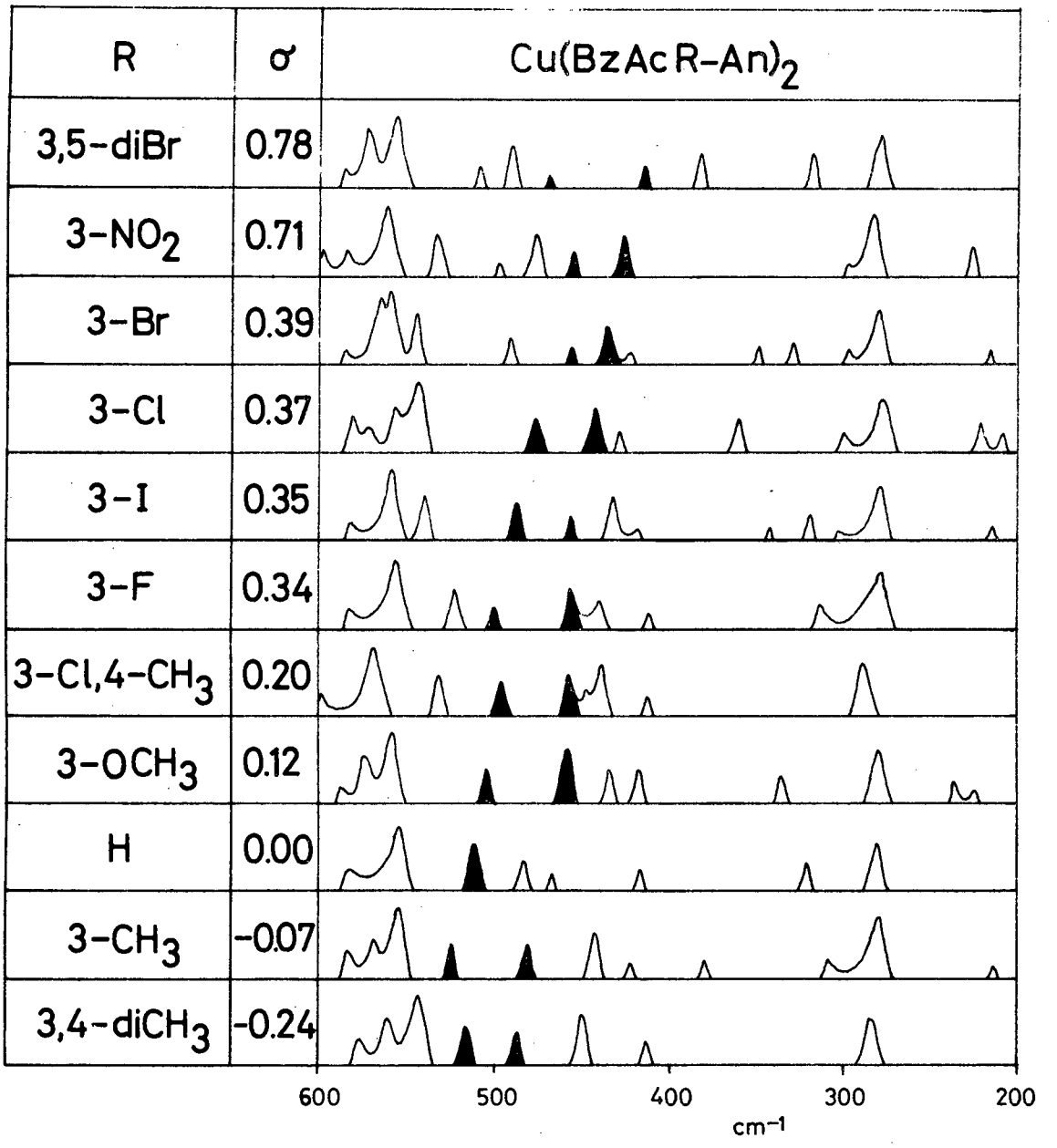


Figure 10. The infrared spectra of 3-substituted Cu(II) benzoylacetanilide complexes, 200 - 600 cm^{-1}. Solid peaks : νCu-O.

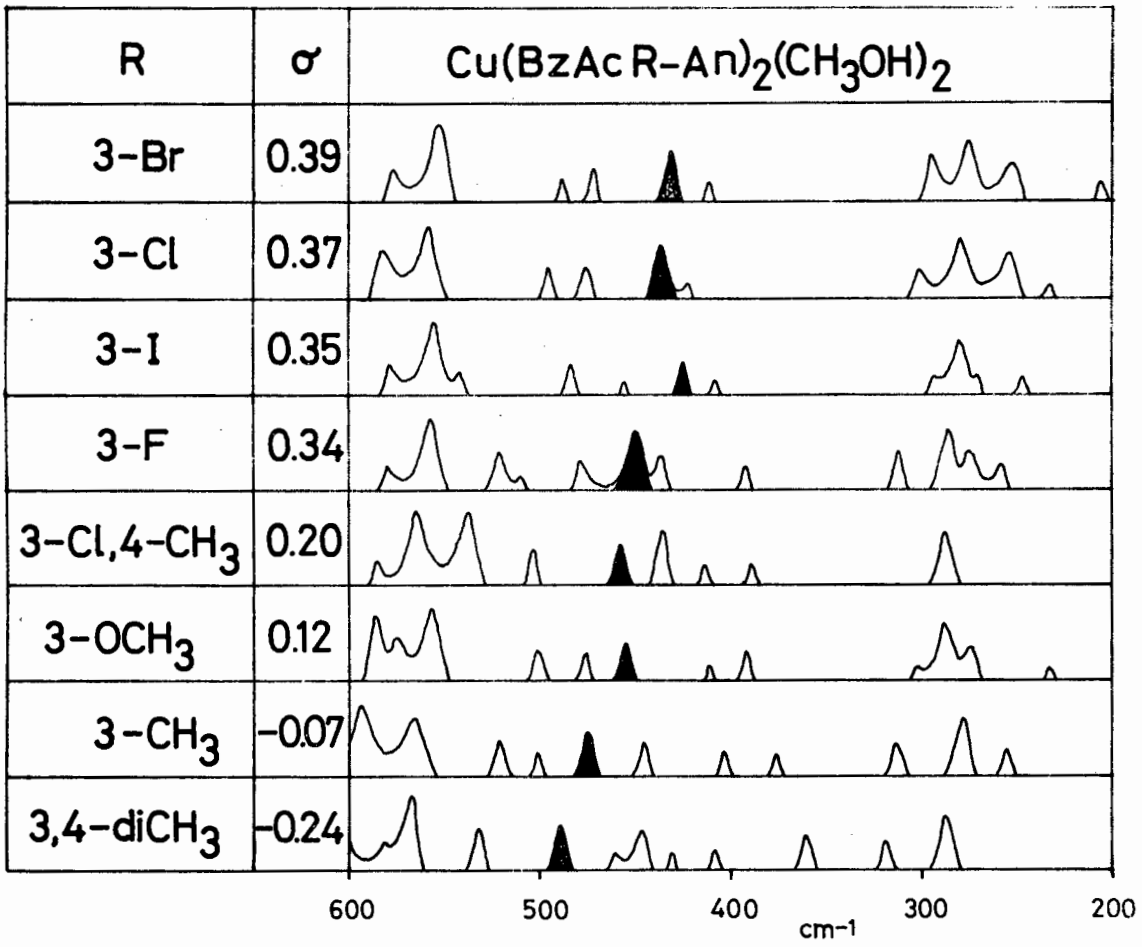


Figure 11. The infrared spectra of the methanol adducts of 3-substituted Cu(II) benzoylacetanilide complexes, 200 - 600 cm^{-1}. Solid peaks : νCu-O.

Table 78. νCu-O for the copper benzoylacetanilide complexes $Cu(BzAcR\text{-}An)_2$ and their methanol adducts $Cu(BzAcR\text{-}An)_2(CH_3OH)_2$

R	σ	νCu-O	
4-substituted complexes			
$4\text{-}NO_2$	0.78	457	446
4-CN	0.63	485	472
$4\text{-}COCH_3$	0.52	496	489
4-I	0.28	501	
4-Br	0.23	503	495
4-Cl	0.23	505	498
4-F	0.06	525	512
H	0.00	510	
$4\text{-}NHCOCH_3$	-0.01	527	511
$4\text{-}OC_6H_5$	-0.03	517	
$4\text{-}CH_3$	-0.17	530	513
$4\text{-}OCH_3$	-0.27	550	524
3-substituted and 3,4-disubstituted complexes			
$3\text{-}NO_2$	0.71	454	426
3-Br	0.39	457	436
3-Cl	0.37	478	442
3-I	0.35	488	456
3-F	0.34	498	458
$3\text{-Cl},4\text{-}CH_3$	0.20	495	456
$3\text{-}OCH_3$	0.12	506	459
$3\text{-}CH_3$	-0.07	524	479
$3,4\text{-di}CH_3$	-0.24	516	485
Adducts			
3-Br	0.39	432	
3-Cl	0.37	437	
3-I	0.35	425	
3-F	0.34	450	
$3\text{-Cl},4\text{-}CH_3$	0.20	457	
$3\text{-}OCH_3$	0.12	455	
$3\text{-}CH_3$	-0.07	477	
$3,4\text{-di}CH_3$	-0.24	490	

Electronic Spectra.

The electronic spectra of metal β-ketoenolate complexes have been widely studied and reviewed[100]. A number of semi-empirical Hückel and self-consistent field calculations have been carried out[101-106]. These yield approximate placement of the energy levels and assignments have been made on the basis of these studies. There has been less agreement on the assignments in the spectra of β-ketoenolate complexes of Cu(II) than in those of other metal ions. It is generally accepted that the intense absorption near 33 kK arises from a $\pi_3 \rightarrow \pi_4^*$ transition and that the weak absorption in the range 14 - 20 kK originates in the $d \rightarrow d$ transitions. The assignment of the intense band near 40 kK and less intense bands, appearing as shoulders on the $\pi_3 \rightarrow \pi_4^*$ bands, have been the source of some disagreement. The band near 40 kK was assigned[101] to the $\pi_3 \rightarrow \pi_5^*$ transition but the assignment was subsequently altered[103-105] to the $\sigma_L \rightarrow 3d_{xy}$ charge transfer transition. Evidence favouring the latter assignment was the insensitivity[107] (unlike the $\pi_3 \rightarrow \pi_5^*$ band) of the frequency of this band to solvent coordination and substitution on the γ-carbon atom and the observation that it was shifted in relation to the inductive effects of the α-substituents[103].

The electronic spectra of the benzoylacetanilide complexes (Figure 12 , Tables 55 and 56) show the general characteristics of Cu(II) β-ketoenolate spectra with two intense bands (with molar absorptivities ε about 45,000 in methanol) near 30 and 40 kK and weak absorption (ε about 65) near 15 kK. They also show a moderately intense band or shoulder (ε about 12,000) near 35 kK and weak shoulders (ε about 200 and 2000 respectively) near 23 and 27 kK. The difference between

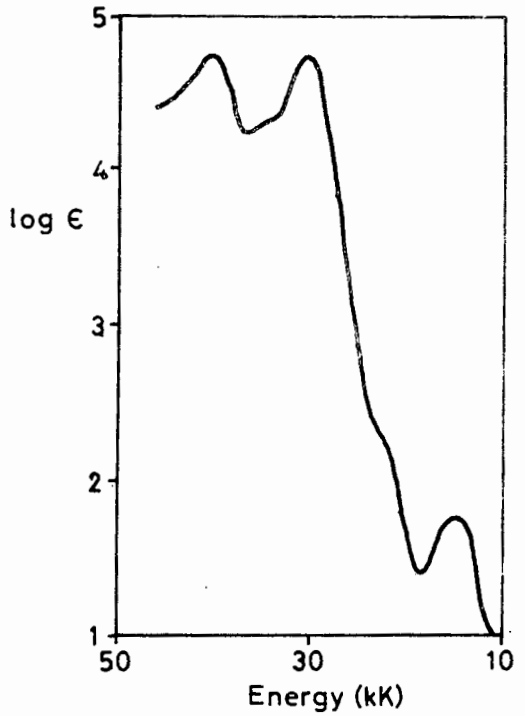


Figure 12. The electronic spectrum of Cu(II) benzoylacetanilide.

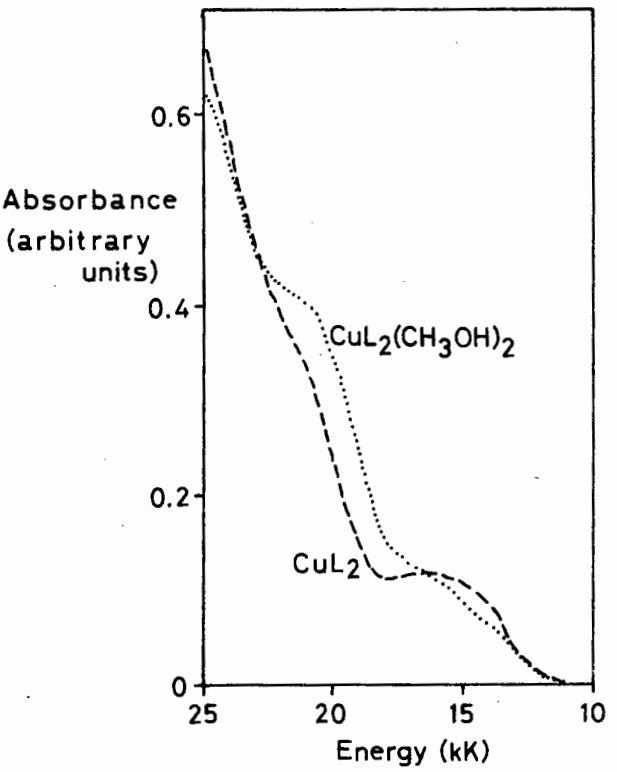


Figure 13. Comparison of the visible electronic spectra of the 3-substituted Cu(II) benzoylacetanilide complexes $[CuL_2]$ and their methanol adducts $[CuL_2(CH_3OH)_2]$.

the complexes and their methanol adducts (Figure 13) is the replacement of the band near 15 kK by a shoulder and increased relative absorption in the region near 20 kK.

The intense band near 30 kK is assigned to one component of the allowed $\pi_3 \rightarrow \pi_4^*$ transition on the basis of its intensity and frequency in relation to those predicted by calculations on various Cu(II) β-ketoenolate molecules[101-106]. This assignment receives support from the observation that the ligands and their sodium salts also yield a band of similar energy and substituent sensitivity to that of the 30 kK band in the copper complexes. A significant shift towards lower energy is induced in this band by the substituents 4-NO_2, 4-CN, and 4-$COCH_3$, other substituents having relatively little effect on its position. A unique feature of these three substituents is that they are the only substituents among those studied which have electron withdrawing effects by a resonance mechanism (Swain and Lupton's resonance parameter, R, provides a suitable index of this measure). Calculations[103] have shown that the $\pi_3 \rightarrow \pi_4^*$ transition should shift to higher energy with increasing Cu-O π-bonding. It would be expected that substituents with electron withdrawing resonance effects would facilitate this π-bonding. It is, however, observed that in the copper benzoylacetanilide complexes, electron withdrawing resonance effects induce a shift towards lower energy, a shift which is similar to that observed in the spectra of the ligands and their sodium salts where no π-bonding is possible. It is therefore deduced that metal-ligand π-bonding is of minor significance in the copper(II) benzoylacetanilide complexes and that the induced shifts in the $\pi_3 \rightarrow \pi_4^*$ transition energies are determined largely by inductive effects.

That inductive effects are predominantly operative is reasonable in view of the absence of conjugation between the anilide and chelate rings and is also consistent with previous observations that substitution of the methyl groups of Cu(II) acetylacetonate by trifluoromethyl groups induces a shift in the $\pi_3 \rightarrow \pi_4^*$ transition energy to lower energy.

The band near 35 kK is assigned to the other component of the $\pi_3 \rightarrow \pi_4^*$ transition. This band is observed as a shoulder except for the complexes with substituents 4-NO_2, 4-CN and 4-$COCH_3$ and its energy is thus not determinable with the same accuracy as the component of lower energy.

The band near 40 kK is assigned to the $\sigma_L \rightarrow 3d_{xy}$ charge transfer transition. As deduced in section 2, where the electronic spectra of Cu(II) β-ketoenolate complexes are discussed, when an aromatic ring is present in the ligand, the band occurring near 40 kK is considered to be a composite band with its intensity derived from the $\sigma_L \rightarrow 3d_{xy}$ transition and from a transition associated with the aromatic ring. Anilines yield[268] the p-(^1L_a) band in methanol near 40 kK. This generally compares well with the values for this band in the benzoylacetanilide ligands (Table 58) and their sodium salts (Table 57). The energy of the band is relatively not affected by solvent coordination (Table 59). This is in agreement with work on other copper(II) β-ketoenolate complexes[103,107].

Comparatively low intensity bands near 23 and 27 kK, occurring as shoulders on the 30 kK band, are generally observed in the Cu(II) benzoylacetanilide spectra. Syamal[155] cited the occurrence of these bands in the spectrum of the unsubstituted complex as evidence of Cu-Cu

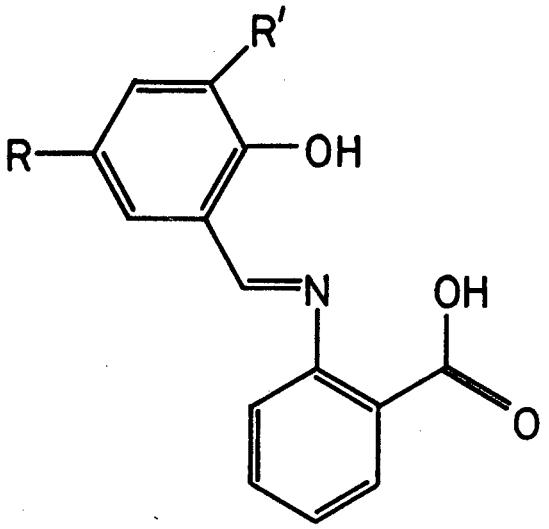
interaction. However, reports that the presence of a band near 27 kK is associated with Cu-Cu interaction is invalidated by its appearance in the spectra of several Cu(II) β-ketoenolate complexes with normal magnetic moments[103,200,310]. This band has been assigned to a spin-forbidden $\pi \rightarrow \pi^*$ transition or $n \rightarrow \pi^*$ transition[103], a charge transfer $\pi \rightarrow 3d$ transition[310] and a charge transfer $3d \rightarrow \pi^*$ transition[104,105]. The assignment remains uncertain, but the $3d \rightarrow \pi^*$ assignment is the most probably correct.

A broad envelope containing the four $d \rightarrow d$ bands is observed within the range 14 - 20 kK in Cu(II) β-ketoenolate spectra[105]. In methanol, the Cu(II) benzoylacetanilide complexes exhibit an asymmetrical envelope of weak intensity (molar absorptivity ε about 65) near 15 kK. In some of the reflectance spectra two bands near 14 and 17 kK are partially resolved. In various solvents the position of the absorption maximum is in the order benzene>chloroform>acetone>ethanol>methanol>pyridine (Table 60). This shift towards lower energy with increasing coordinating power of the solvent molecules is understandable since solvent coordination will raise the d_{z^2}, d_{xz} and d_{yz} orbital energies relative to the $d_{x^2-y^2}$ orbitals and thus move the absorption maximum of the band to lower energy.

4. N-SALICYLIDENEANTHRANILATE COMPLEXES: THE EFFECT OF ^{15}N-LABELLING, METAL ION SUBSTITUTION AND LIGAND SUBSTITUTION ON THEIR INFRARED AND ELECTRONIC SPECTRA.

The physical properties of metal complexes of N-salicylideneanthranilic acids have not been widely studied. The limited extent of investigation probably arises, in common with the metal complexes of Schiff bases generally, from the variety of structures which the complexes form, the uncertainty of the coordination geometry, the impracticability of applying normal coordinate methods to the assignment of bands in the infrared spectra and the complexity of the infrared spectra which results from the presence of phenyl vibrations, at least three different metal-ligand bonds and extensive vibrational coupling. The infrared spectra of the Ni and Cu complexes have only been reported[186,187] for the region above 1500 cm^{-1} while the spectra of the Co and Zn complexes have not been reported at all. Electronic spectra have been reported for some Ni and Cu complexes[186,187] and the 2,2'-bipyridine and 1,10-phenanthroline adducts of Cu complexes[194,195] but have not been reported for Co complexes. Magnetic moments for some Ni complexes[186], a number of Cu complexes[179,184,187] and their adducts[194,195] and a single Co complex[179] have been determined.

In this section the application of ^{15}N-labelling, metal ion substitution and the effect of varying the ligand substituents to the assignment of bands in the infrared spectra of the complexes (X) is discussed. The stereochemistry of the complexes is discussed in relation to the infrared and electronic spectroscopic results and



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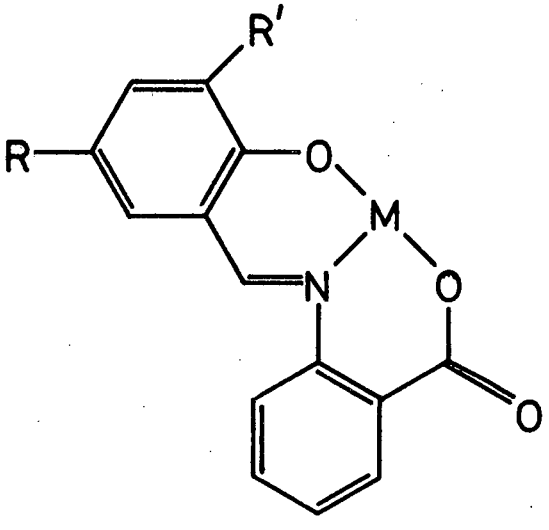


(X)

magnetic moment determinations. The infrared spectra are given in Tables 28 to 33, the electronic spectra in Tables 62 to 64 and the magnetic moments in Table 68. Typical electronic spectra are shown in Figures 16 and 18. The infrared spectra are shown in Figures 19 to 22.

The N-salicylideneanthranilic acids themselves have been very little studied. The infrared and electronic spectra have not been reported. The infrared spectrum and ^{15}N-induced shifts of N-salicylideneanthranilic acid are given in Table 27 and the spectrum is shown in Figure 14. The electronic spectroscopic results are given in Table 61 and the electronic spectrum is shown in Figure 15.

There is considerable difficulty in making reliable empirical assignments in the infrared spectra of Schiff bases owing to the extensive vibrational coupling that occurs. ^{15}N-labelling provides an approach to obtain reliable assignments and to enable the relative purity of the vibrational bands to be determined. Here the significant vibrations which shift on ^{15}N-labelling in the infrared spectrum of N-salicylideneanthranilic acid are discussed.

There are two ^{15}N-sensitive bands (Table 27, Figure 14) at 1599 and 1570 cm^{-1} in the spectrum of N-salicylideneanthranilic acid. The higher frequency band is found to be sensitive to metal ion substitution. The lower frequency band does not appear in the spectra of all the compounds and is absent from the spectra of the metal complexes. Both bands are assigned to $\nu C{=}N$. The observed isotopic shifts of -2.3 and -2.2 cm^{-1}, respectively, are small, since a

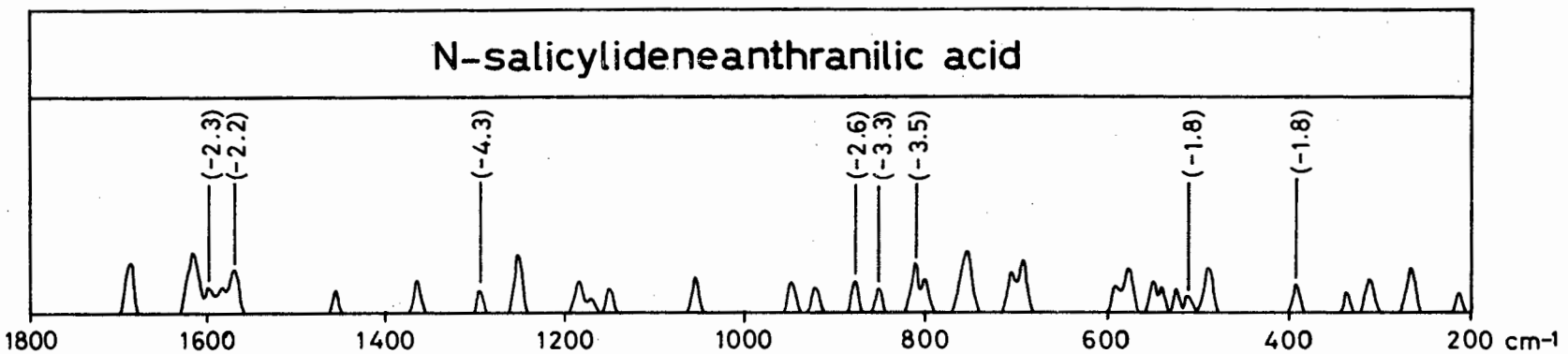


Figure 14. The infrared spectrum of N-salicylideneanthranilic acid.
Figures in parentheses are shifts (cm^{-1}) induced by ^{15}N-labelling.
For all other bands the shifts are <1.5 cm^{-1}.

maximum ^{15}N-induced shift of -40 cm^{-1} is expected[311] for an uncoupled $\nu C{=}N$ band. It is clear that there is extensive coupling in both vibrations. The degree of coupling is evidently greater than in N-4-tolylsalicylaldimine, where shifts of -5 and -8 cm^{-1} are reported[15].

The band at 1294 cm^{-1} is assigned to $\nu C{-}N$ by virtue of its shift on ^{15}N-labelling and its position. The bands between 810 and 880 cm^{-1}, which exhibit isotopic shifts of between -2.6 and -3.5 cm^{-1}, are assigned to bending vibrations associated with the C=N-C skeleton. Bands in these parts of the spectrum have been similarly assigned[15] in N-4-tolylsalicylaldimine.

A band which is not sensitive to ^{15}N-labelling appears at 1620 cm^{-1}. Its position and absence of ^{15}N-sensitivity suggest its assignment to the aromatic ring stretching frequency normally found near 1600 cm^{-1}. The band at 1690 cm^{-1} is assigned, by virtue of its position, to $\nu C{=}O$. In aromatic acids $\nu C{-}O$ is found[312] near 1350 cm^{-1}. In N-salicylideneanthranilic acid the band at 1366 cm^{-1} is assigned to $\nu C{-}O$ of the carboxyl group. The phenolic $\nu C{-}O$ will probably occur at a lower frequency than the carboxyl $\nu C{-}O$ and it is suggested that the band at 1248 cm^{-1} is assigned to $\nu C{-}O$ of the phenolic group.

The electronic spectrum of N-salicylideneanthranilic acid shows a weak band at 24.1 kK and intense bands at 30.3 and 39.2 kK (Table 61 and Figure 15). It is suggested that the two intense bands result from $\pi \rightarrow \pi^*$ or benzenoid transitions.

In general the empirical formulae of the complexes are CoL, CuL, ZnL and $NiL(H_2O)$ (H_2L = R-salanth). These formulae apply

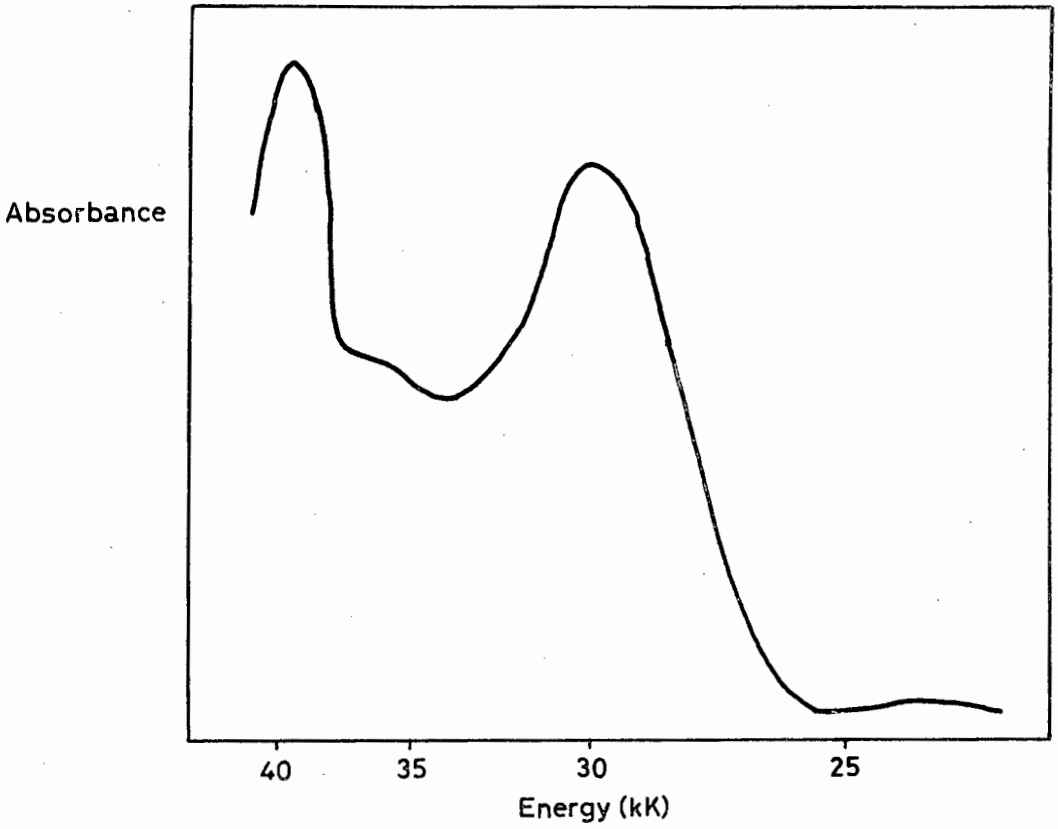


Figure 15. Electronic spectrum of N-salicylideneanthranilic acid in methanol solution.

to all complexes in which the salicylidene ring is monosubstituted except for Zn(5-CH_3salanth) which is isolated as the hemihydrate. When the salicylidene ring is disubstituted a number of different hydrated species are found for the Co, Cu and Zn complexes. The Ni complexes, however, have microanalysis figures which correspond most closely with the formula NiL(H_2O)(Table 6).

The magnetic moments of the Co complexes all lie within the range 4.30 to 4.59 Bohr magnetons. Those with a monosubstituted salicylidene ring have moments in the range 4.30 to 4.41 Bohr magnetons (Table 68). These values all lie within the accepted range for tetrahedral coordination of the Co(II) ion[237,313,314]. Confirmation of the structure of the monosubstituted complexes is obtained from the electronic reflectance spectra (Figure 16). These complexes show a very broad band centred at about 6 kK and three other bands near 11, 14 and 18 kK. This band pattern is similar to those of the thiourea complexes of Co(II)[315,316] and of $Hg[Co(SCN)_4]$[317] which have tetrahedral stereochemistry. The band near 6 kK is assigned to the $^4T_{1g}(F) \leftarrow {}^4A_2$ transition. The presence of this band in the spectrum, together with the values of the magnetic moments, is conclusive evidence that these complexes have tetrahedral symmetry. The assignment of the other bands is not clear but one of them can be assigned to the $^4T_1(P) \leftarrow {}^4A_2$ transition[318].

The disubstituted complexes (Figure 17) do not show this pattern, having a band near 6 kK but only one band in the region 8 to 20 kK. This band pattern is indicative of a tetrahedral arrangement of donor atoms, but in the absence of the broad band near 6 kK and the

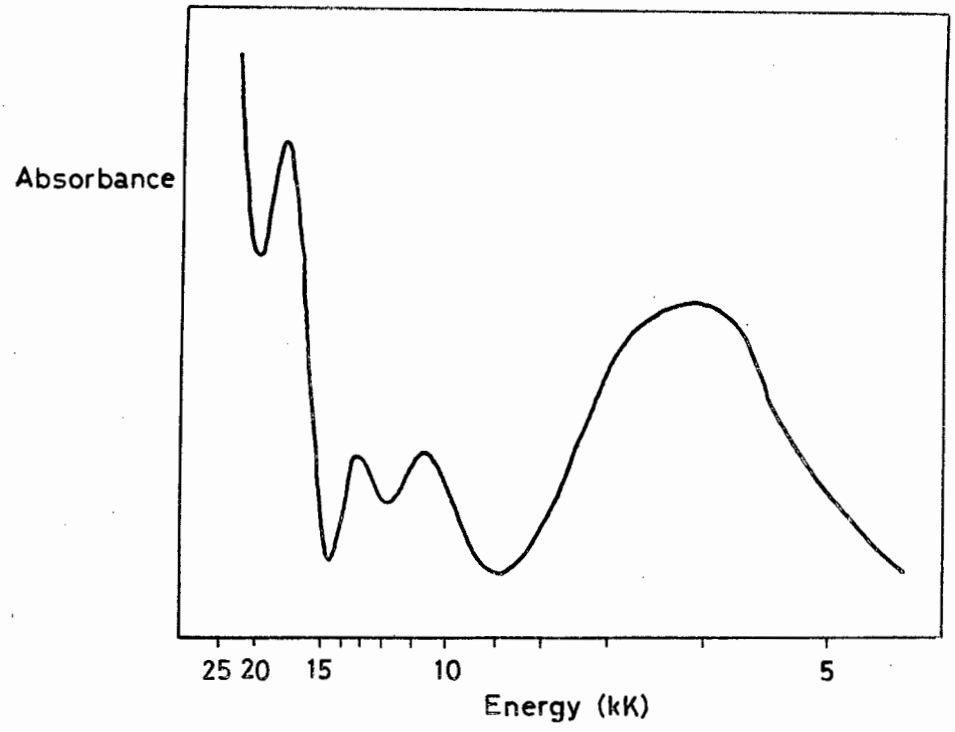


Figure 16. Reflectance electronic spectrum of Co(salanth).

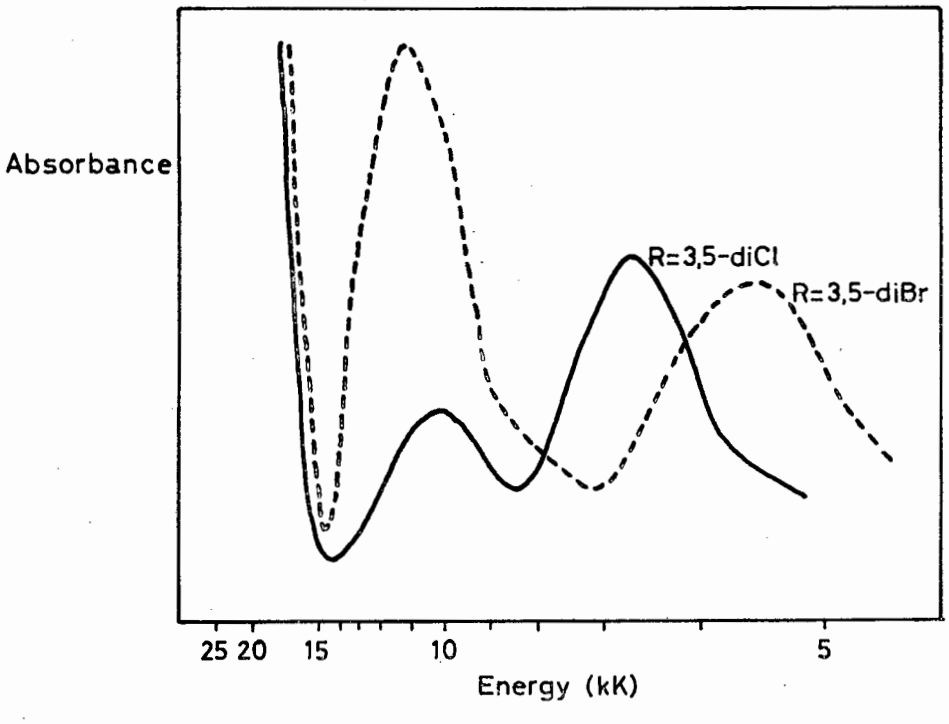


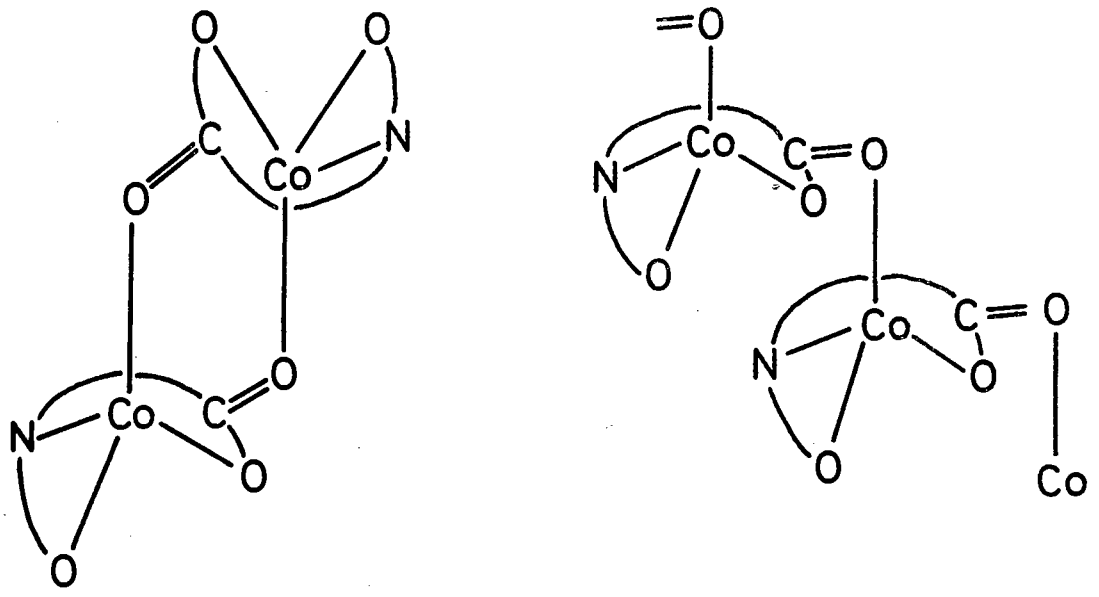
Figure 17. Reflectance electronic spectra of Co(R-salanth).

presence of water molecules in the compounds, the possibility of octahedral stereochemistry cannot be ruled out.

The infrared spectra of the Zn complexes show an almost exact one-for-one band correspondence with the analogous Co complexes and it is therefore concluded that the Zn complexes also have a tetrahedral structure. For tetrahedral coordination to occur the ligand must bond to the metal ion through the salicylidene and carboxyl oxygen atoms (from which protons have been lost) and the nitrogen atom, the free carboxyl group then bonding to another metal ion. In this way, dimers or chains are formed with the structures (i) and (ii).

The magnetic moments of the Ni complexes lie within the range 3.28 to 3.45 Bohr magnetons (Table 68). The electronic spectra generally show two bands near 10 kK and 16 kK and a shoulder near 8 kK (Figure 18). It would seem unlikely that tetrahedral coordination occurs since this would require magnetic moments in the range 3.5 to 4.2[313,319] Bohr magnetons and a multiple band in the electronic spectrum near 16 kK[318]. The magnetic moments and the electronic spectra are indicative of octahedral coordination but a five-coordinate structure cannot be ruled out, especially as the empirical formula is $NiL(H_2O)$.

Octahedral Ni complexes have magnetic moments in the range 2.8 to 3.4 Bohr magnetons[237,313,319] and their electronic spectra have three bands, one within each of the ranges 7 kK to 13 kK ($^3T_{2g} \leftarrow {}^3A_{2g}$), 11 kK to 20 kK ($^3T_{1g} \leftarrow {}^3A_{2g}$) and 19 kK to 27 kK ($^3T_{1g}(P) \leftarrow {}^3A_{2g}$)[318]. The N-salicylideneanthranilate complexes show three distinct bands at about 10 kK, 16 kK and 24 kK corresponding to these three transitions, the highest, because of its proximity to a band in the ligand spectrum,



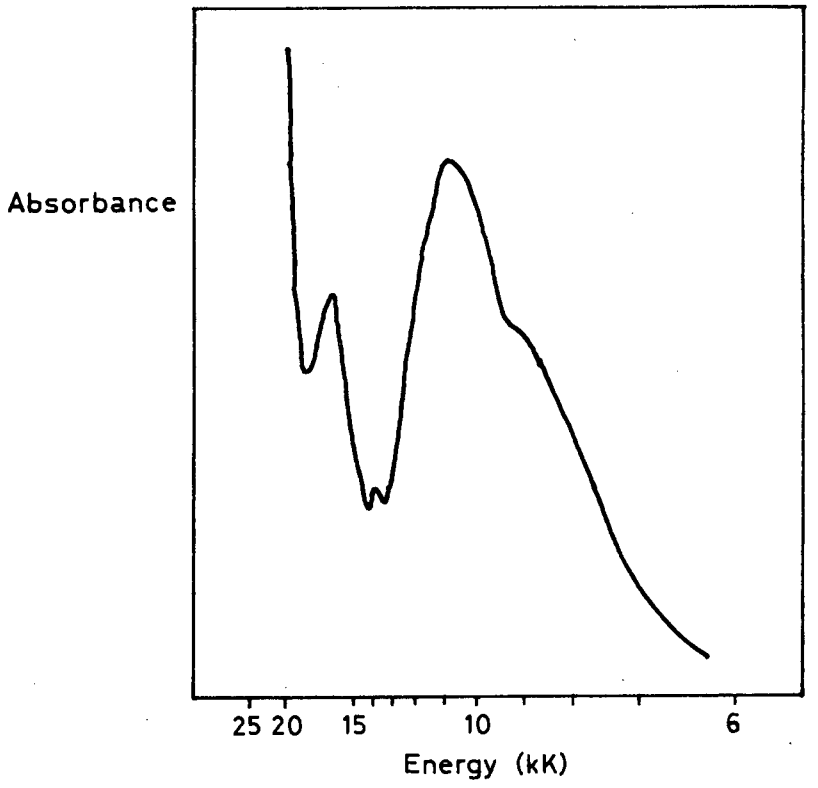
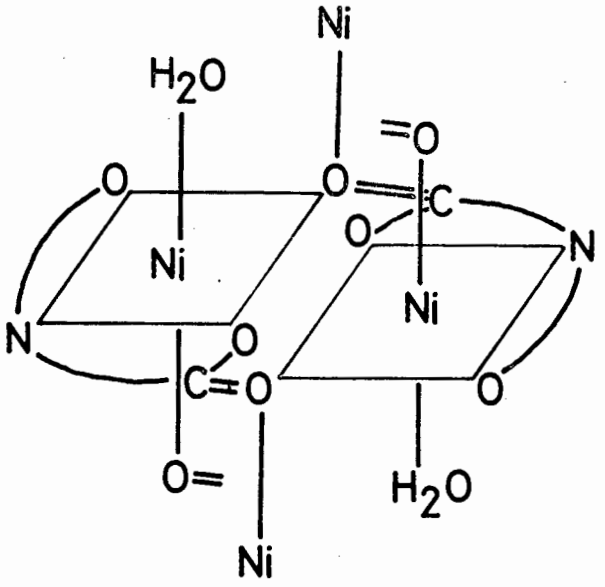


Figure 18. Reflectance electronic spectrum of Ni(5-Clsalanth).

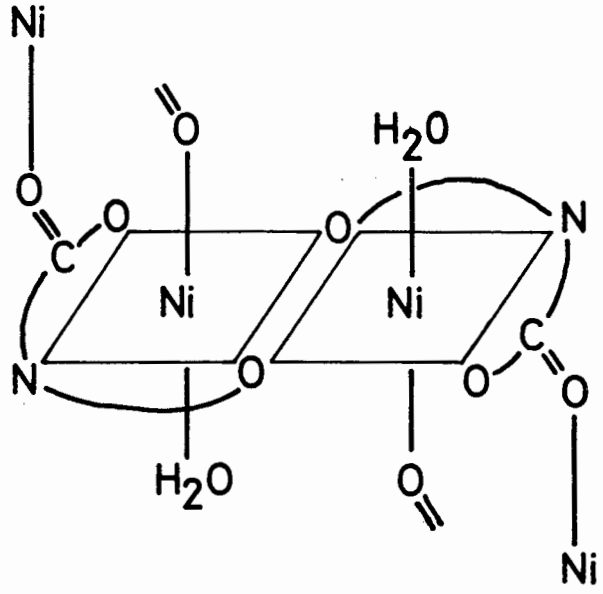
presumably being a composite band. The 5-Cl substituted compound exhibits a weak band at 13.4 kK which may be assigned to the spin-forbidden $^1Eg \leftarrow {}^3A_{2g}$ transition sometimes observed at approximately this energy in octahedral Ni complexes[318]. Majumdar and Bhattacharyya[186] observed bands in $NiL(NH_3)$ at 11.0, 18.4 and 25.8 kK, assigning them to the $^3T_{2g} \leftarrow {}^3A_{2g}$, $^3T_{1g}(F) \leftarrow {}^3A_{2g}$ and charge transfer transitions, respectively. They concluded from these data and a magnetic moment of 2.71 Bohr magnetons that the complex contains octahedrally coordinated nickel.

In order to account for the octahedral coordination of the nickel ions it must be assumed that oxygen atoms bridge between nickel ions. Either the salicylidene oxygen atom or the carboxyl oxygen atom can be visualized as bonded to two different nickel ions, with possible structures (iii) and (iv).

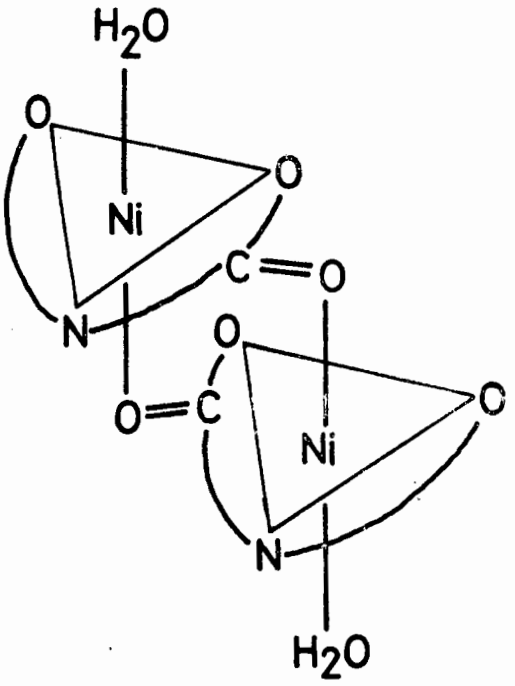
Structures similar to those postulated for the Co complexes can be put forward for the Ni complexes if the Ni ion is taken to be five-coordinate with a trigonal bipyramidal arrangement of donor atoms. On magnetic and electronic spectroscopic evidence a structure of this type is possible. Five-coordinate nickel complexes have magnetic moments in the same range[320-322] as those found for the N-salicylidene-anthranilate complexes. Experimental results[322,323] and theoretical calculations[324,325] indicate that three bands between 6 kK and 20 kK should occur in the electronic spectra of five-coordinate nickel ions. The experimental results (Table 63) do possibly show three bands in this region. It is clear that a firm decision as to whether the Ni ion in Ni N-salicylideneanthranilate complexes is five- or six-coordinate


Ni
H2O
O
O
C
O
N
Ni
Ni
N
O
C
O
O
O
O=
H2O
Ni

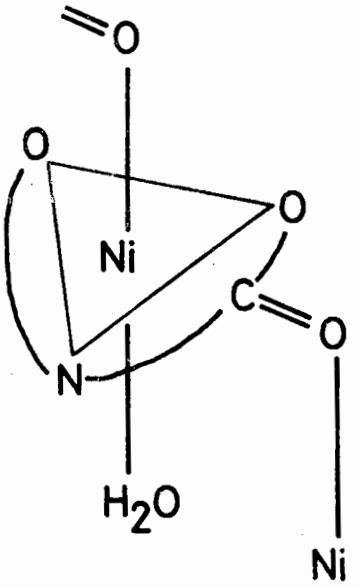
(iii)


Ni
O
H2O
O
O
N
C
Ni
Ni
C
N
O
O
O
H2O
O
Ni

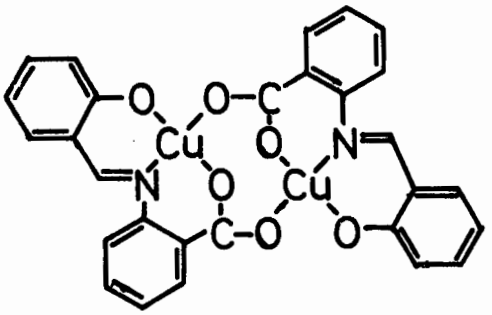
(iv)



(v)



(vi)



(vii)

cannot be made from the magnetic moments and electronic spectra. If the structure is trigonal bipyramidal assumption of bridging by oxygen atoms is unnecessary. Dimers or chains will be formed with structures (v) and (vi).

Any proposed structures for the copper complexes must account for their magnetic moments. By analogy with N-salicylidene-2-aminophenol complexes which have subnormal magnetic moments, the N-salicylidene-anthranilate complexes are also expected to have a subnormal moment. However, the magnetic moments of the copper complexes[179,184] (Table 68) are within the normal range for one unpaired electron. To account for this fact Kubo *et al.*[184] proposed a dimeric structure (vii) with square planar four-coordinate Cu atoms in an eight-membered ring with each carboxyl oxygen atom bonded to the Cu atom of the other molecule. In any other alternative bridged dimeric structure, a four-membered ring would be formed and a subnormal magnetic moment would be expected[200]. A normal magnetic moment has also been found for the copper N-salicylidene-β-alanine complex and an eight-membered ring structure has also been proposed for this compound[192].

The structures of the complexes are thus:
Co and Zn tetrahedral, Ni octahedral (or possibly trigonal bipyramidal) and Cu square planar.

The infrared spectra and ^{15}N-induced shifts of the N-salicylideneanthranilic acid complexes are given in Table 28 and shown in Figure 19 . The ^{15}N-induced shifts of the Ni complex were not able to be determined below 590 cm^{-1} owing to the absence of an identical band pattern in this region for the labelled and unlabelled complexes.

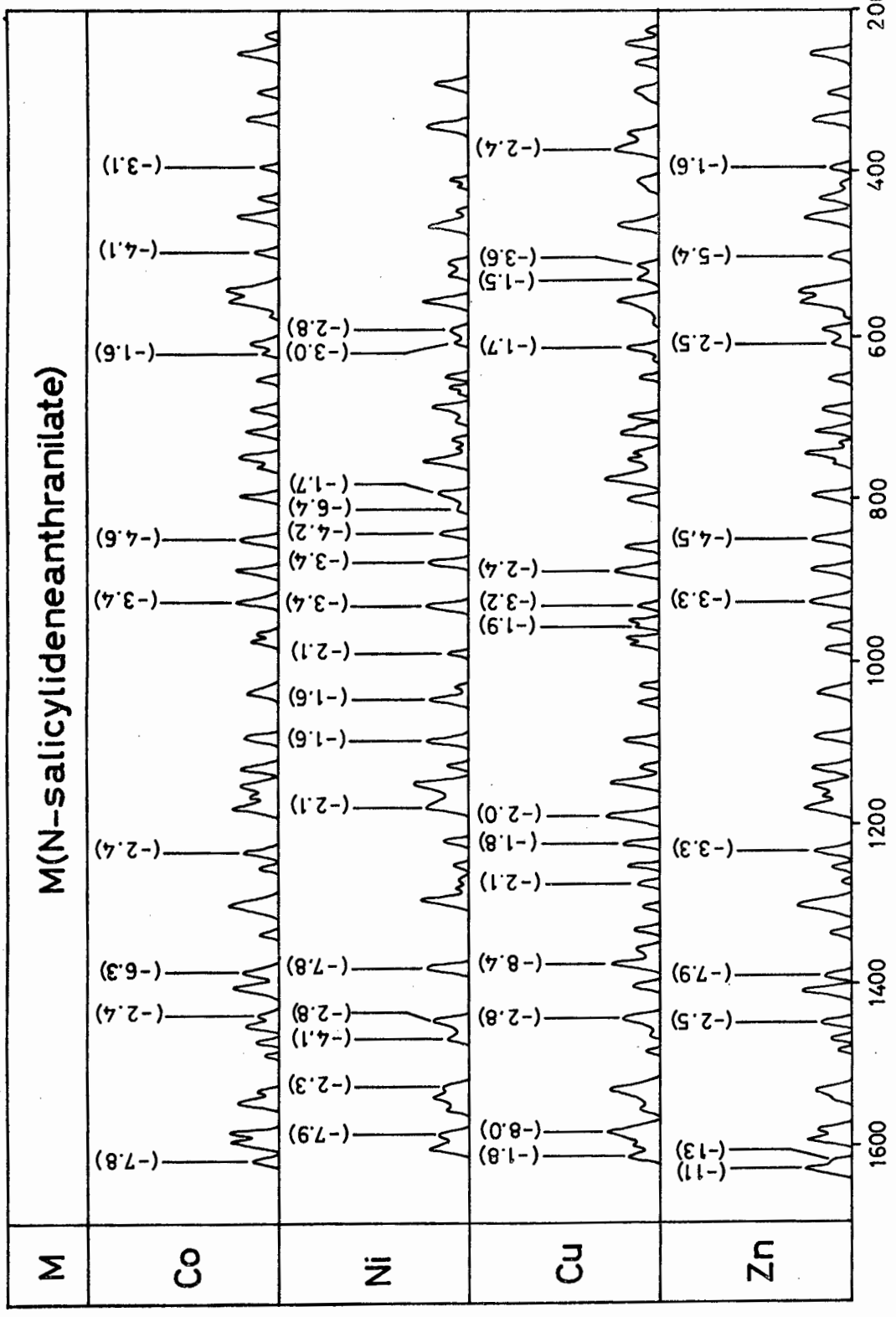


Figure 19. The infrared spectra of the Co(II), Ni(II), Cu(II) and Zn(II) N-salicylideneanthranilate complexes.
Figures in parentheses are shifts (cm^{-1}) induced by ^{15}N-labelling.
For all other bands the shifts are <1.5 cm^{-1}.

This feature could be due to differing amounts of water in the crystal lattice, with a consequent change of structure, although both compounds were made in exactly the same way and gave analytical results corresponding to an empirical formula $NiL(H_2O)$.

The most striking feature of the spectra concerns the ^{15}N-sensitive bands near 1600 cm^{-1}, where the frequencies of the Co and Zn complexes are considerably higher than those of the Ni and Cu complexes. The order of frequencies is Co>Ni>Cu<Zn (which is the reverse of the Irving-Williams stability order[259]). This band is assigned to νC=N. The Cu complex has another band showing slight ^{15}N-sensitivity at a higher frequency than more ^{15}N-sensitive band. This band, together with a shoulder at lower frequency in the Zn complex is also assigned to νC=N. That considerable coupling occurs, is indicated by the observed shifts of about -8 cm^{-1} compared with -40 cm^{-1} expected[311] for uncoupled νC=N. However, there is considerably less coupling than occurs in the ligand.

A band showing large ^{15}N-sensitivity occurs near 1385 cm^{-1} and one with a smaller ^{15}N-induced shift near 1450 cm^{-1}. These bands are both assigned to coupled νC-N, the band of lower frequency being vibrationally purer. This latter band essentially parallels the behaviour of νC=N in its metal sensitivity, having frequencies in the order Co>Ni~Cu<Zn.

It is clear from the infrared spectra of the complexes, as no band is present above 1635 cm^{-1}, that the oxygen atom of the carboxyl group is externally bonded. The vibrational frequencies of the carboxylate group (-COO) in various compounds have been studied by a number of workers[312,326-332]. It is considered that the positions of

the two stretching vibrations of this group and the separation between them are indicative of the nature of the bonding involving the carboxyl oxygen atoms. McAuliffe and Perry suggested[332] that the separation between the two frequencies depends on the symmetry of the carboxyl group. In ionically bonded compounds such as the alkali metal salts of carboxylic acids the bands occur[331] at about 1530 and 1390 cm^{-1} with a separation of about 150 cm^{-1}. In sodium anthranilate, for example, they occur[12] at 1532 and 1398 cm^{-1} with a separation of 134 cm^{-1}. In compounds where one oxygen atom is covalently bonded to a hydrogen atom or alkyl group, they occur at more widely separated values - 1770 and 1284 cm^{-1} with a separation of 486 cm^{-1} in gaseous acetic acid[330] and at 1650 and 1344 cm^{-1} with a separation of 306 cm^{-1} in bis(picolinic acid N-oxide)copper(II)[312]. Where both oxygen atoms are bonded either to metal ions or hydrogen bonded to water molecules, the separation of the bands and the frequency of the higher band will be intermediate between the two extremes, becoming closer to the ionically bound case as the ketonic oxygen atom is more strongly bound. Thus, in metal anthranilate complexes[12], the bands appear in the ranges 1553 to 1571 cm^{-1} and 1377 to 1413 cm^{-1} with a separation of about 150 cm^{-1}. This indicates that the ketonic oxygen is strongly bound to another metal ion. In contrast, in anhydrous α-amino acid complexes[331,332], the bands appear in the ranges 1583 to 1620 cm^{-1} and 1366 to 1420 cm^{-1} with a separation of about 210 cm^{-1}, indicating that interaction between the ketonic oxygen atom and metal ion is not as strong as in the anthranilate complexes. Confirmation of the assignments of the carboxyl group vibrations arises from the study of the infrared spectrum of ^{18}O-labelled glycine[333] where bands which are ^{18}O-sensitive occur at

1604 cm^{-1} and 1413 cm^{-1}, that is, with a separation of 191 cm^{-1}.

In the N-salicylideneanthranilate complexes an intense broad band appears near 1545 cm^{-1}. This band is not sensitive to ^{15}N-labelling and is assigned to one of the stretching vibrations of the carboxyl group, νCOO. A band in the region near 1300 cm^{-1} is assigned to the other stretching vibration. These assignments agree with those reported in the spectra of metal anthranilate[12,329] and α-amino acid complexes[331,332]. The separation of about 145 cm^{-1} and the rather low value of the frequency of the higher band is firm evidence that, in N-salicylideneanthranilate complexes, the ketonic oxygen is strongly bound, presumably to a metal ion.

The phenolic C-O stretching frequency has been assigned[15] in metal salicylaldimine complexes to bands in the region 1300 - 1350 cm^{-1}. No band is observed in this region in the Ni complex and since it would be expected that this νC-O would have a frequency lower than that found for the carboxylate stretching vibrations, the bands in the region of 1220 cm^{-1} and 1250 cm^{-1} are assigned to the phenolic C-O stretching frequency. Since these bands show a small ^{15}N-sensitivity, some coupling with a mode involving the nitrogen atom apparently occurs.

A number of bands between 800 and 950 cm^{-1} show quite considerable ^{15}N-induced shifts. These bands are assigned, as in the salicylaldimine complexes[15], to various bending vibrations of the C=N-C skeleton.

In section 1, where the infrared spectra of metal halide aniline complexes was discussed, it was found that νM-N was higher for the square

planar Cu complex than for the tetrahedral Co and Zn complexes. Thus, in the series of complexes discussed here, which also have the structures Cu square planar and Co and Zn tetrahedral, the probably order of frequencies is Co<Cu>Zn.

Below 620 cm^{-1} there are three sets of bands which show considerable ^{15}N-sensitivity. The bands near 500 cm^{-1} show the largest ^{15}N-induced shifts and the frequencies lie in the order Co<Cu>Zn (Figure 20). This band is therefore assigned to the vibrationally purest (least coupled) metal-nitrogen stretching vibration. The order of frequencies of this band is the opposite of those assigned to νC=N and νC-N. Thus, stabilization of the M-N bond is accomplished at the expense of the adjacent C=N and C-N bonds.

The other two bands below 620 cm^{-1} showing smaller ^{15}N-sensitivity and a metal dependency that is either small or does not follow the sequence Co<Cu>Zn (namely those near 390 cm^{-1} and 610 cm^{-1}) may be assigned to less pure νM-N. The bands near 340 cm^{-1} showing no or little ^{15}N-sensitivity and a metal dependence in the order Co<Cu>Zn may be assigned to a mode which is predominantly νM-O.

Two other complexes were ^{15}N-labelled, namely the Co and Cu complexes of N-5-methylsalicylideneanthranilic acid. The Zn complex was not labelled, since the Zn complex of the unsubstituted ligand showed the same pattern of ^{15}N-induced shifts as was observed in the Co complex. It will be assumed that with this ligand the Zn and Co complexes will also have the same pattern of ^{15}N-induced shifts. The infrared spectra are given in Table 29 and shown in Figure 21 .

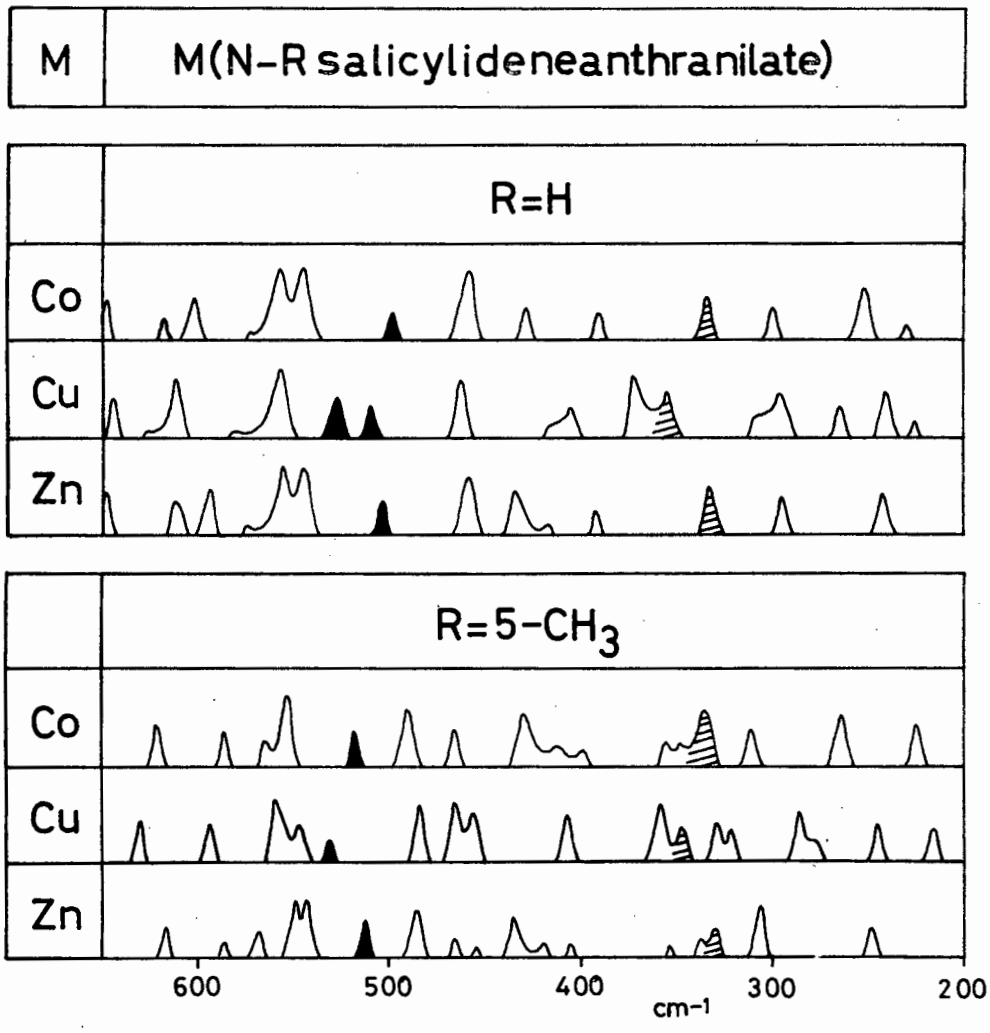


Figure 20. Effect of metal ion substitution on the infrared spectra of metal(II) N-Rsalicylideneanthranilate complexes. Solid peaks : νM-N; shaded peaks : νM-O.

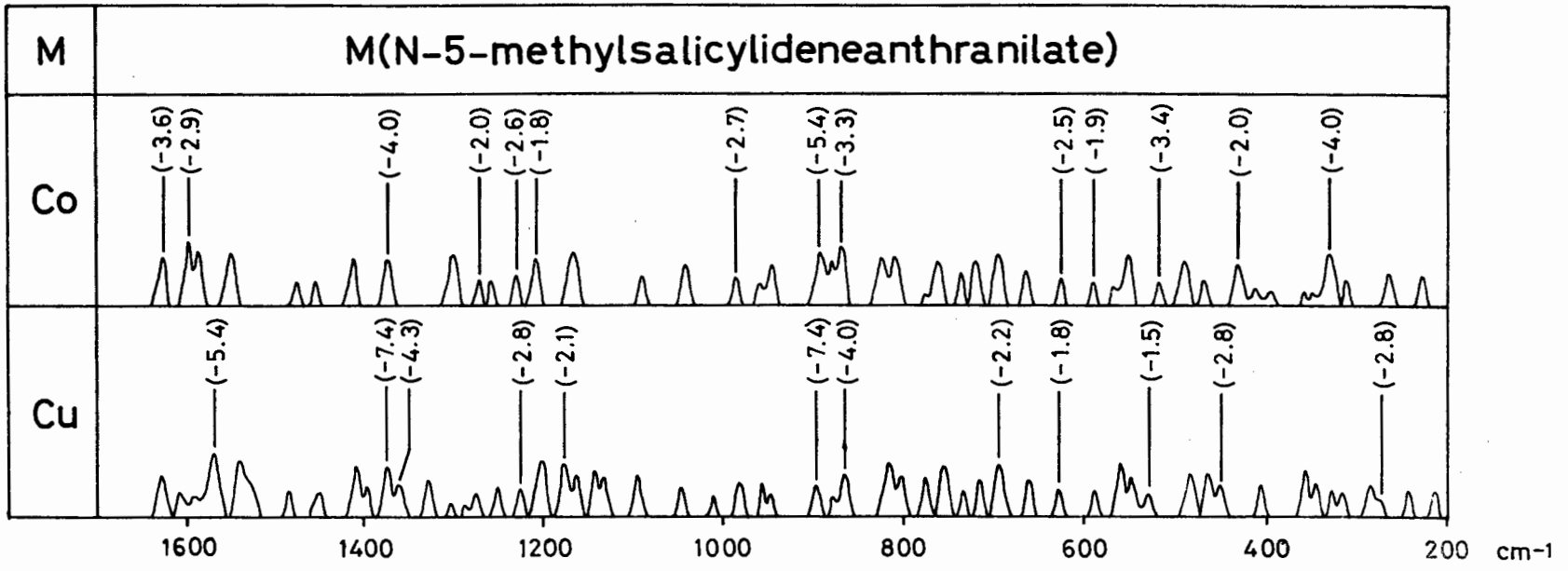


Figure 21. The infrared spectra of the Co(II) and Cu(II) N-5-methylsalicylideneanthranilate complexes.

Figures in parentheses are shifts (cm^{-1}) induced by ^{15}N-labelling.
For all other bands the shifts are $<1.5\ cm^{-1}$.

In the region between 650 cm^{-1} and 1650 cm^{-1}, essentially the same pattern of ^{15}N-sensitive bands occurs in these complexes as in the unsubstituted complexes discussed above. Bands assigned to νCOO are again observed near 1300 cm^{-1} and 1550 cm^{-1}. In the region below 650 cm^{-1}, the bands near 520 cm^{-1} show ^{15}N-induced shifts and a frequency order Co<Cu>Zn. These bands are therefore assigned to νM-N. The bands near 450 and 620 cm^{-1} may be assigned to less vibrationally pure νM-N while the bands near 340 cm^{-1} may be coupled vibrations predominantly νM-O.

It has frequently been found that the metal-ligand stretching frequencies in metal complexes are shifted by substitution in the ligand (R-sensitive bands). Good correlations have been found between parameters which measure the electronic effects of the substituents and νM-L in a number of systems[12,15]. A number of N-salicylideneanthranilate complexes substituted in the salicylidene ring has been prepared. The infrared spectra between 200 and 650 cm^{-1} are shown in Figure 22 for the Co and Cu complexes (X: M = Co or Cu; R" = H; R' = NO_2, Cl, H, CH_3).

It is seen that the band, assigned to the vibrationally purest νM-N by ^{15}N-labelling in the unsubstituted and 5-CH_3 substituted compounds, is shifted by substitution with the frequency order 5-NO_2<5-Cl<H<5-CH_3. This order is found for both the Co and Cu complexes and in the Zn complexes prepared, bands are found in this region with an order 5-Cl<H<5-CH_3. This order of frequencies follows the sequence of pure inductive effects or of their combined inductive-resonance effects (as given by σ_p or σ_m). It definitely does not follow the sequence of any available pure resonance parameter.

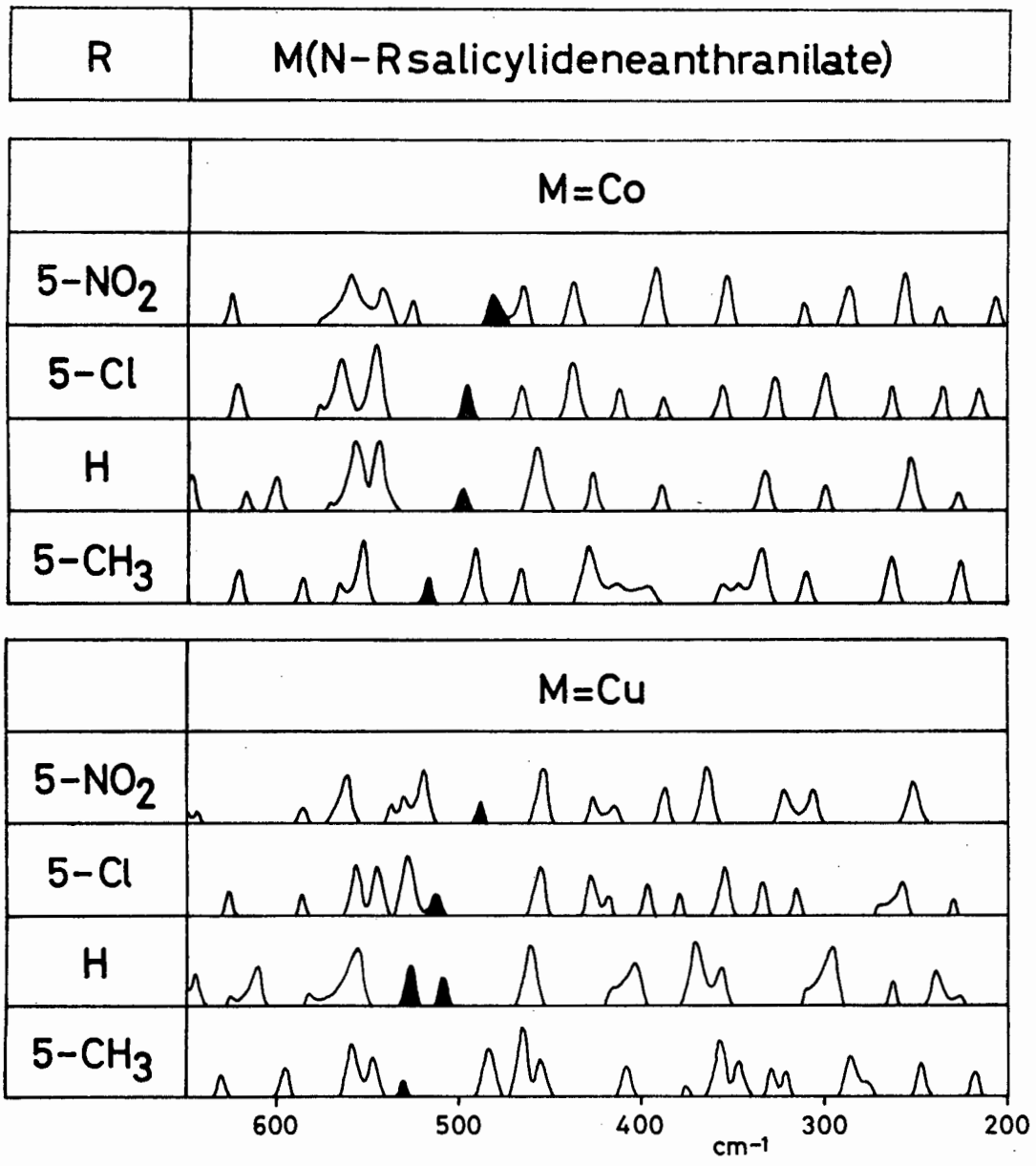


Figure 22. The infrared spectra of substituted Co(II) and Cu(II) N-salicylideneanthranilate complexes, 200 - 650 cm^{-1}. Solid peaks : νM-N.

Assignment of bands in the infrared spectra of the 3,5-dihalogen substituted complexes was not deemed feasible. Absence of a common stoichiometry with that of the 5-substituted complexes, with the possibility of a different stereochemistry (as is indicated by the electronic spectra of the 3,5-dihalogen substituted Co complexes) renders reliable assignments difficult. Further studies on this set of complexes must await the results of isotopic labelling.

5. BENZOYLARYLIDENEHYDRAZONE COMPLEXES : THE EFFECT OF METAL ION SUBSTITUTION AND LIGAND SUBSTITUTION ON THEIR INFRARED AND ELECTRONIC SPECTRA.

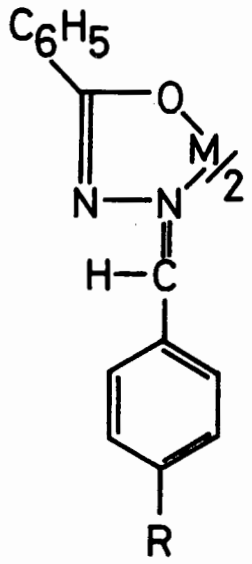
Benzoylbenzilidenehydrazone complexes.

The infrared spectra of metal complexes of benzoylbenzilidene-hydrazones (XI) have not been widely studied. Previous work[205,208] has been concerned with the characterization of the different complexes formed by reaction of the ligands with metal chlorides or metal acetates. The infrared spectra of metal benzoylbenzilidenehydrazones have not been reported below 1200 cm^{-1}.

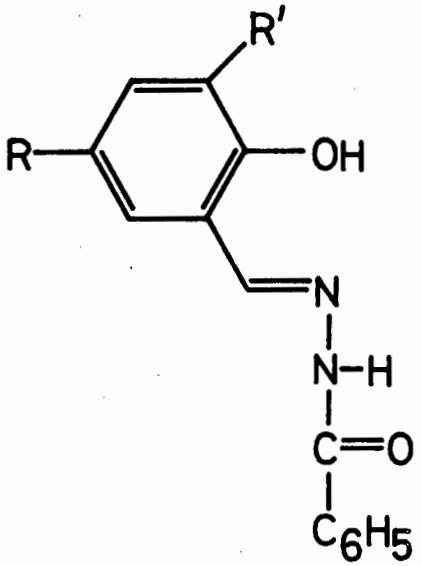
In this section the effect of metal ion substitution and the effect of varying the ligand substituents is discussed with a view to assignment of the bands in the infrared spectra. The infrared spectra are given in Tables 34 and 35 .

The ligands react with metal acetates in the enolic form, losing one proton, and forming a five-membered chelate ring (XI). It was found possible only to prepare analytically pure compounds when the substituent on the benzilidene ring was a hydrogen atom or a group with electron releasing properties. The Ni complexes are orange and have been reported[205] to be diamagnetic. They have been assumed to be square planar. The Cu complexes are dark brown.

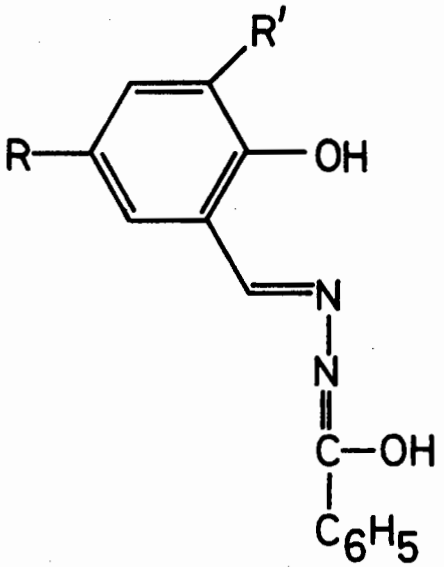
The infrared spectra between 200 and 650 cm^{-1} are shown in Figure 23 . There is a good band for band correspondence for the complexes of each metal, indicating that the structures are the same



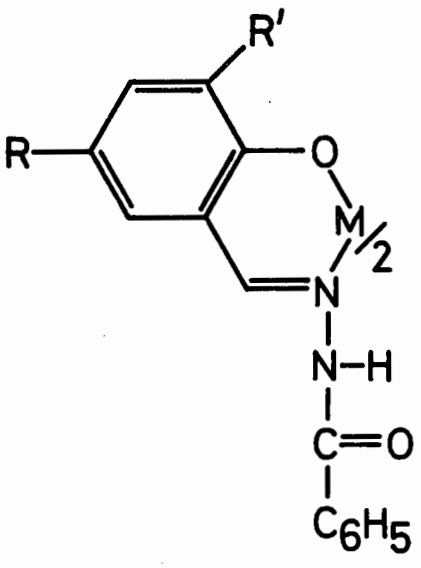
(XI)



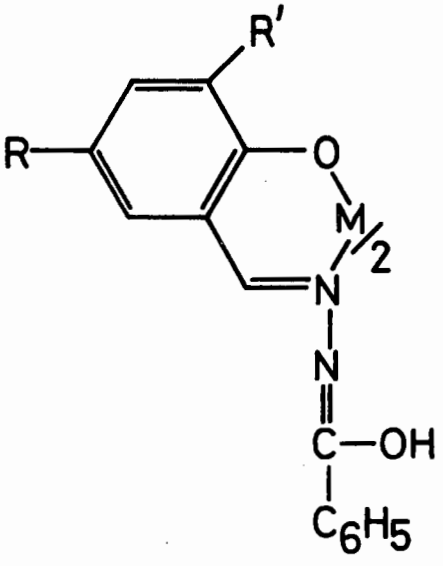
(XII)



(XIII)



(XIV)



(XV)

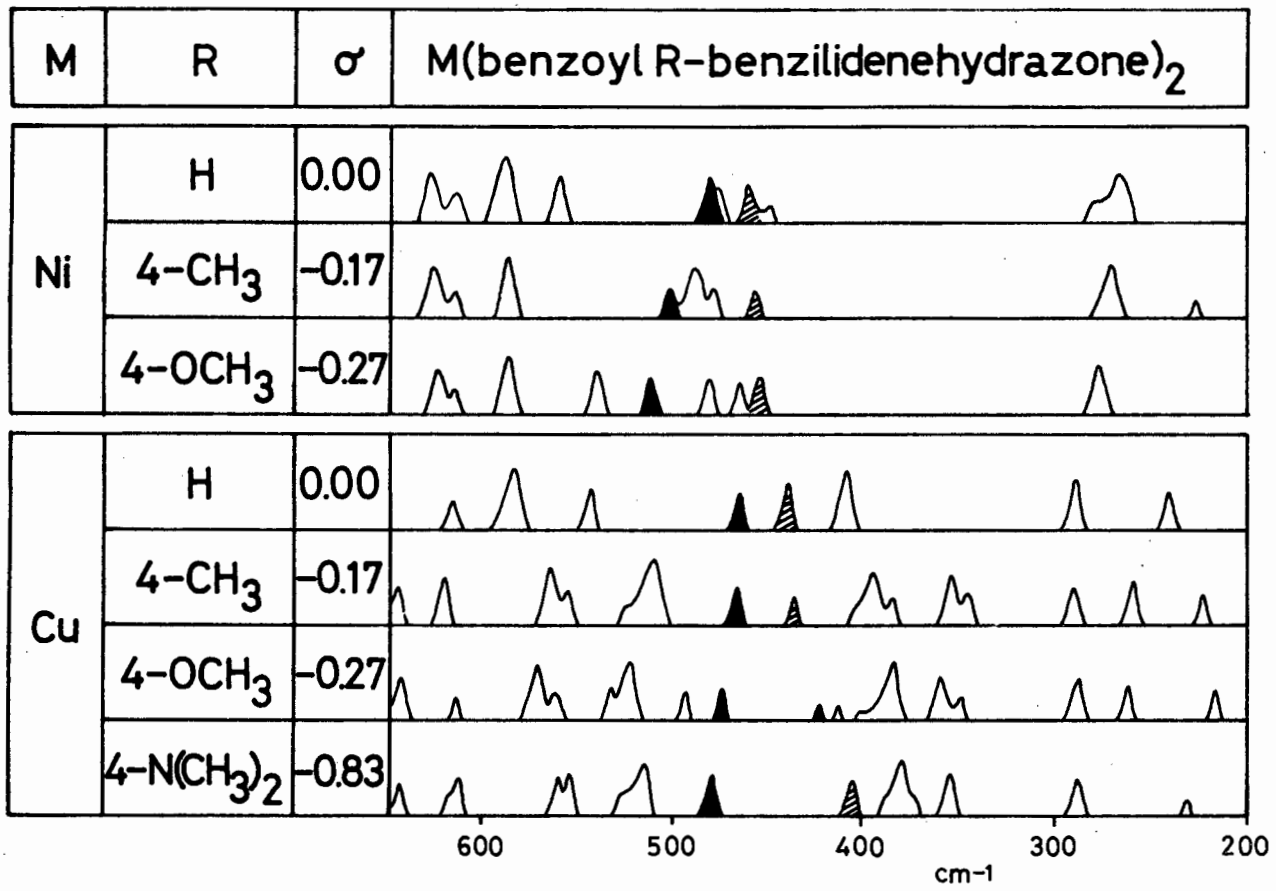


Figure 23. The infrared spectra of 4-substituted Ni(II) and Cu(II) benzoylbenzilidenehydrazone complexes, 200 - 650 cm^{-1}. Solid peaks : νM-N; shaded peaks : νM-O.

for each compound. Examination of the infrared spectra shows that there is a band in the range 465 - 510 cm^{-1} in each set of complexes which is moved to higher frequency by increasing electron withdrawal of the substituents. Furthermore, in each pair of complexes having the same substituent, this band is at a higher frequency in the Ni complex than in the Cu complex. This is the order to be expected from theoretical considerations for square planar complexes, since the highest antibonding orbital is occupied in the Cu(II) ion and is vacant in the Ni(II) ion. This order of frequencies, Ni>Cu, has been shown previously[8,15] for square planar N-arylsalicylaldimine and β-ketoenolate complexes. This band is therefore assigned to a metal-ligand vibration and is probably νM-N, as this vibration would be more reasonably expected than νM-O to be shifted by substitution on the benzilidene ring. Owing to the absence of bands in the spectra of the nickel complexes between 280 and 450 cm^{-1}, a band between 450 and 465 cm^{-1} is most reasonably assigned to νM-O in the nickel complexes and a band in the range 410 to 440 cm^{-1} to νM-O in the Cu complexes. The band shown in Figure 23, which moves to lower frequency on increasing electron withdrawal of the substituent, is tentatively assigned to νM-O. The opposite shifts of these two bands with change of substituent indicates that increase in the bond order of the M-N bond is at the expense of the M-O bond.

Bis(benzoylsalicylidenehydrazone) complexes.

The complexes formed formally by the reaction of two singly deprotonated benzoylsalicylidenehydrazone molecules with a metal(II) ion have only been reported[209,210] for nickel. Magnetic moments were

reported but no infrared or electronic spectra have been published. In this section, the magnetic properties and infrared and electronic spectra of the Co(II), Ni(II), Cu(II) and Zn(II) complexes of benzoylsalicylidenehydrazones will be discussed with a view to characterising their structure and assigning bands in the infrared spectra.

Benzoylsalicylidenehydrazone (BSH) may exist as keto-enol tautomers. That the keto form (XII) exists in the solid state is seen from the strong band in the infrared spectrum at 1657 cm^{-1}. This does not exclude the existence in the solid state of the enol form (XIII). Coordination of the ligand with a metal ion to form an $M(HL)_2$ (H_2L=BSH) species can take place in two ways. In the first, the enol proton is lost and the keto-enol oxygen and the azomethine nitrogen atom bond with the metal ion, forming a five-membered ring. The complexes would have a structure analogous to the benzoylbenzilidenehydrazone complexes (XI). In the second, the phenolic proton is lost and this oxygen atom and the azomethine nitrogen atom bond with the metal ion, forming a six-membered ring. With this structure there is also the possibility of keto-enol tautomerism (XIV) and (XV). Sacconi considers[209] that the complexes exist in the enolic form (XV) on the grounds that they are soluble in sodium hydroxide solution and are reprecipitated by acetic acid or carbon dioxide. That a free keto group does not exist in the complexes is seen from the fact that no strong band is found in the infrared spectra above 1629 cm^{-1}.

The electronic spectra are given in Tables 65 and 66 and the infrared spectra in Tables 37 to 40 . The electronic spectra are shown in Figures 24 and 25 and the infrared spectra between 200 and 650 cm^{-1} are shown in Figure 26.

The magnetic moments are given in Table 69 .

The nickel complexes exhibit bands in the regions of 10 and 17 kK as well as a much more intense band near 23 kK (Figure 24). The bands near 10 and 17 kK are typical of an octahedrally coordinated Ni(II) ion[318]. They are assigned to the $^3T_{2g} \leftarrow {}^3A_{2g}$ and $^3T_{1g} \leftarrow {}^3A_{2g}$ transitions respectively. The band near 23 kK may be assigned to the $^3T_{1g}(P) \leftarrow {}^3A_{2g}$ transition. The cobalt complexes exhibit a band near 9 kK as well as a much more intense band near 23 kK (Figure 25). The spectrum is not typical of a tetrahedrally coordinated Co(II) ion and the band at 9 kK may be assigned to the $^4T_{2g} \leftarrow {}^4T_{1g}$ transition of an octahedrally coordinated Co(II) ion[318]. The band near 23 kK may be assigned to the $^4T_{1g}(P) \leftarrow {}^4T_{1g}$ transition.

The magnetic moments of the nickel complexes (Table 69) are within the accepted range for octahedrally coordinated Ni(II) ions[313,319]. Two of the cobalt complexes (Table 69) have magnetic moments within the range reported for octahedrally coordinated Co(II) ions[313,334]. Although the other two Co complexes have moments close to the spin-only value for the three unpaired electrons, the infrared spectra (see below), nevertheless, indicate that their structures are analogous to those of the nickel complexes and are thus also octahedral.

Examination of the infrared spectra below 650 cm^{-1} (Figure 26) shows that for each ligand, the spectra have very similar band patterns for all the metal ions. This would indicate that the complexes of Co(II), Ni(II) and Zn(II) have the same structure. It is suggested that the metal ions are all octahedrally coordinated having

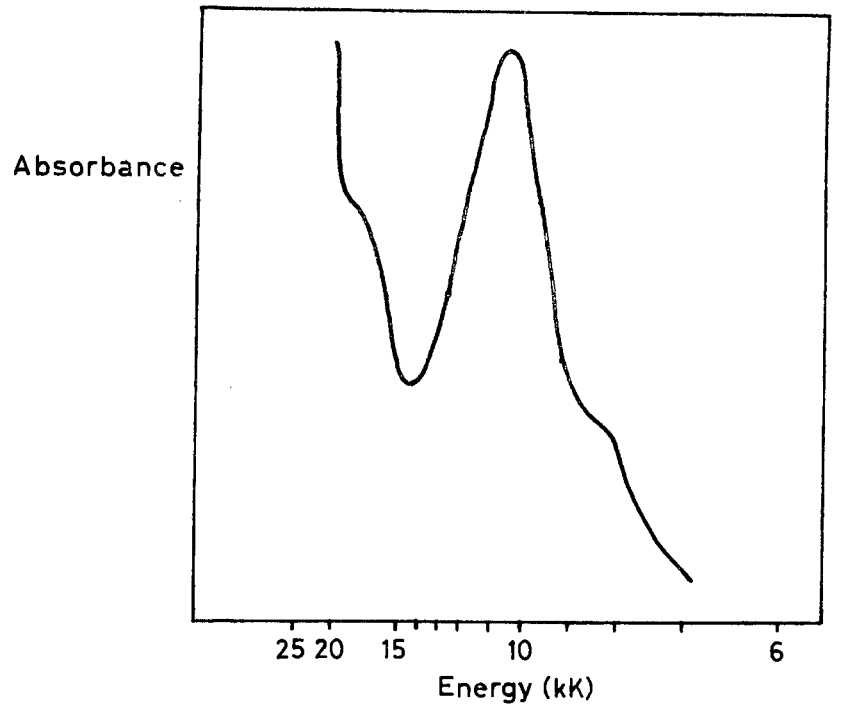


Figure 24. Reflectance electronic spectrum of $Ni(BSH)_2$.

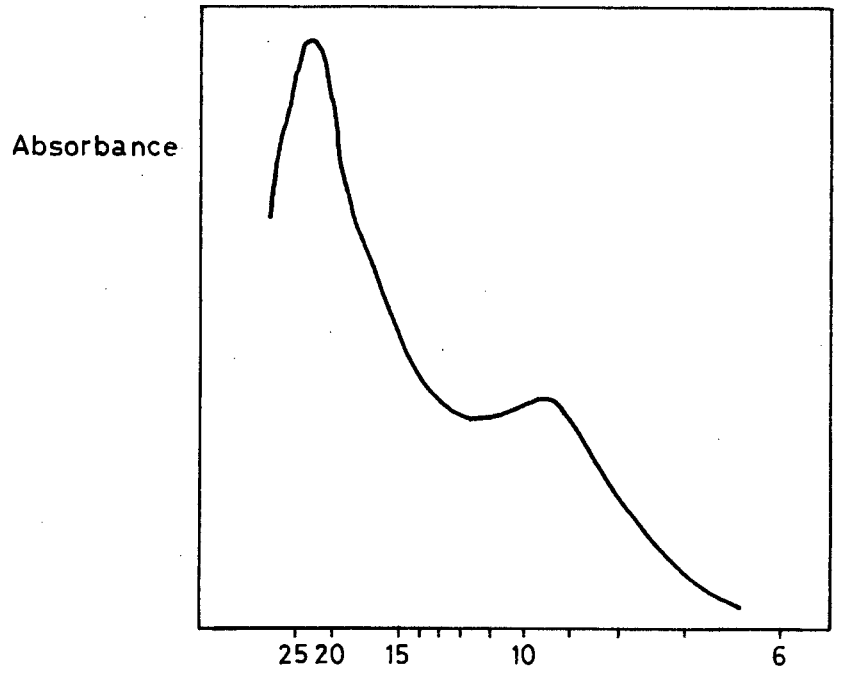


Figure 25. Reflectance electronic spectrum of $Co(BSH)_2$.

a structure involving a six-membered chelate ring (XIV) with the carbonyl oxygen bound to ions in planes above and below the coordination plane.

The analytical data indicate, in most cases, a certain number of water molecules per metal ion. The infrared spectra show diffuse absorption with no definite peaks in the region between 3000 and 3800 cm^{-1}. The fact that the absorption is weak and that usually less than one water molecule is present per metal ion indicates that the water molecules may be hydrogen bonded to the ligands and may not be coordinated to the metal ions.

In the infrared spectra, two bands are found (Figure 26) near 300 cm^{-1} and 480 cm^{-1}, the frequencies of which have a metal dependence in the order Co<Ni>Zn for the complexes (XIV) : R" = H; R' = H,CH_3 or Cl: R'=R"=Cl). This is the order expected for octahedral coordination of all three metal ions. Furthermore, for the complexes with R'=R"=Cl (where the Cu complex was also able to be prepared) a band is present in the spectrum of the Cu complex such that the frequencies have a metal dependence in the order Co<Ni<Cu>Zn which is the Irving-Williams[259] stability order. This indicates that the Cu ions have essentially square planar coordination. This conclusion is supported by the presence of a band in the spectrum of the Cu complex at 1648 cm^{-1}, presumably νC=O, since it occurs at a very similar position in the ligand spectrum. This indicates that in the Cu complex the carbonyl oxygen is not bonded to other Cu ions, in contrast with the other three metal ions. These bands between 290 and 330 cm^{-1} and 460 and 510 cm^{-1} (Table 79) are assigned as the principal metal-ligand stretching vibrations, νM-L.

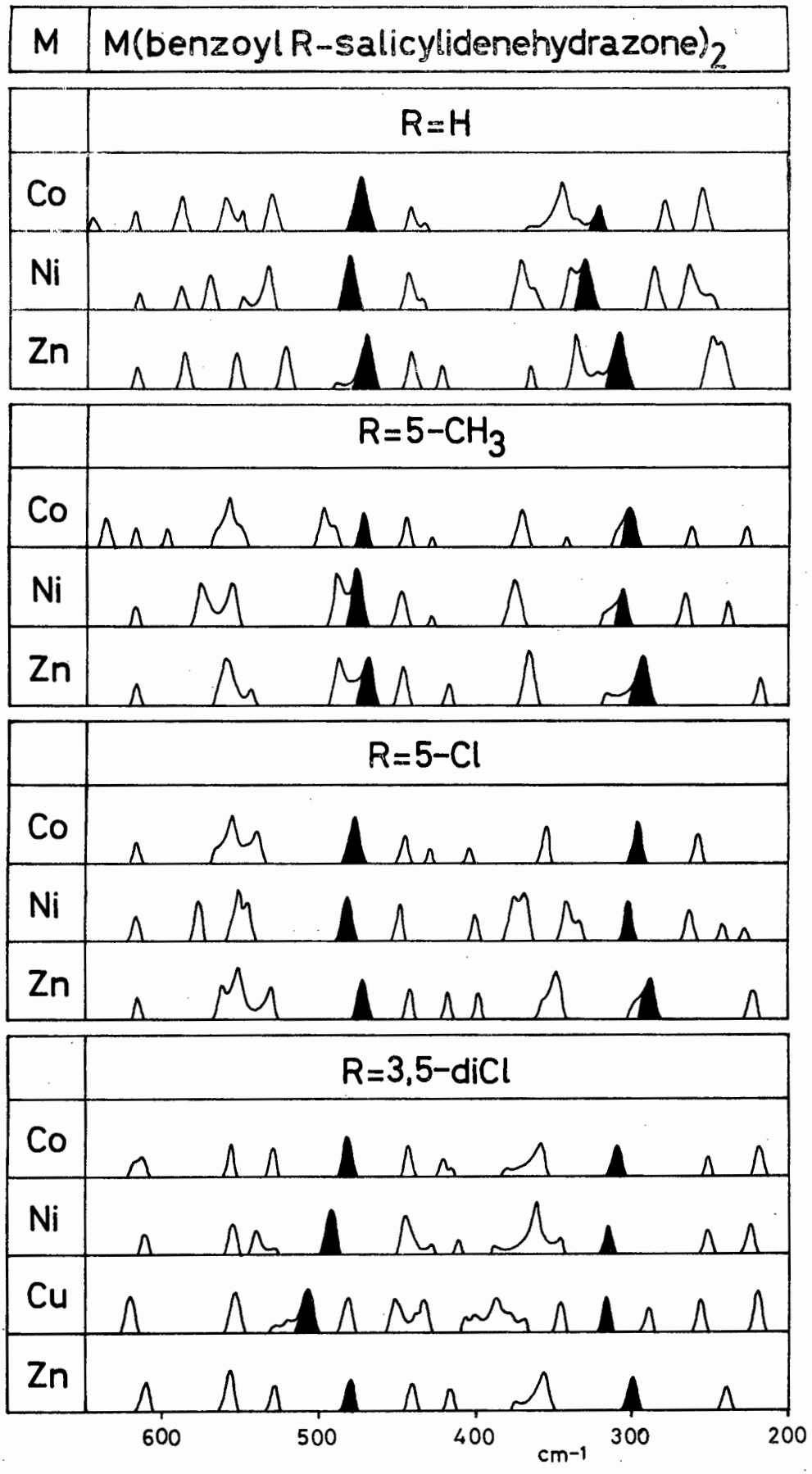


Figure 26. The effect of metal ion substitution on the infrared spectra of metal(II) benzoylsalicylidenehydrazone complexes, 200 - 650 cm^{-1}. Solid peaks : νM-L.

Table 79. Principal metal-ligand stretching vibrations in the metal bis(benzoylsalicylidenehydrazone) complexes. $M(B\text{-}RSH)_2$

M	R → H	5-CH_3	5-Cl	3,5-diCl
Co	322 473	300 472	297 477	310 482
Ni	330 481	307 489	302 482	315 491
Cu				317 510
Zn	309 470	295 469	286 471	301 480

In metal complexes of N-arylsalicylaldimines[15,16] bands have been assigned, on the basis of ^{15}N-labelling, as follows: νC-N between 1380 and 1410 cm^{-1}, and νC=N to two bands between 1580 and 1620 cm^{-1}. In the metal complexes of N-salicylideneanthranilates (Section 4), the corresponding vibrations were assigned, also on the basis of ^{15}N-labelling, to similar regions: νC-N to two bands between 1380 and 1450 cm^{-1}, and νC=N between 1580 and 1635 cm^{-1}. The νC-O (of the phenolic oxygen) has been empirically assigned to a band near 1330 cm^{-1} in the N-arylsalicylaldimine complexes[15,16] and near 1230 cm^{-1} in N-salicylideneanthranilate complexes. The assignment of this band is not conclusive in view of the lack of ^{18}O-labelling studies and the situation is furthermore confused in the N-salicylideneanthranilate complexes by the presence of bands originating in vibrations of the carboxyl group. In the metal complexes of salicyloylsalicylidenehydrazone[214] these bands were assigned empirically as follows: νC=N between 1600 and 1630 cm^{-1}, νC-N near 1380 cm^{-1}, and νC-O near 1250 cm^{-1}. A band between 1600 and 1630 cm^{-1} was also assigned to νC=O (presumably that of the carbonyl group).

In accordance with these earlier assignments, it is suggested that in the metal bis(benzoylsalicylidenehydrazone) complexes, the following assignments may now be proposed. The intense band near 1600 cm^{-1} is assigned to νC=N. It is possible that, in the light of the results on the N-salicylideneanthranilate complexes, the bands in the Ni complexes and the Cu complex near 1560 cm^{-1} should be assigned to this vibration. The band between 1370 and 1390 cm^{-1} is assigned to νC-N, and one of the bands near 1300 cm^{-1} to νC-O. Assignment of a band to νC=O is difficult in view of the uncertainty as to the bond order, but is suggested, from the evidence of the copper complex, that the bond order is such that one of the bands between 1530 and 1580 cm^{-1} or a band near 1625 cm^{-1} may be assigned to this vibration.

Copper benzoylsalicylidenehydrazone complexes.

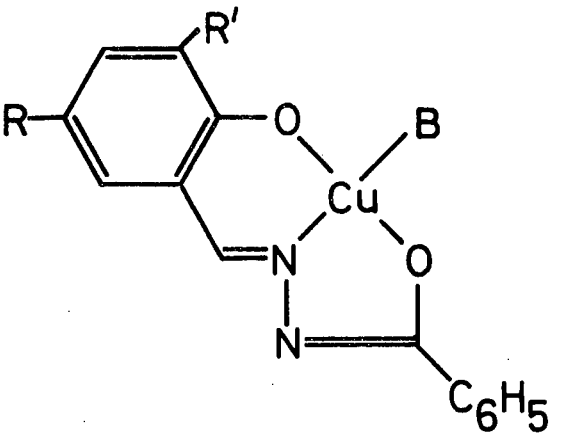
Benzoylsalicylidenehydrazones react with copper acetate in ethanolic ammonia solution to form complexes (XVI) which generally have the empirical formula $CuL(NH_3)(H_2O)$ (H_2L = benzoylsalicylidenehydrazone). When these complexes are heated under reduced pressure at about 130°C for 24 hours complexes having the empirical formula CuL are formed. α-Diimine adducts with the formula CuL(N-N) (N-N = 2,2'-bipyridine or 1,10-phenanthroline) may also be prepared from the latter compounds or directly by mixing copper acetate, the ligand and the α-diimine.

The properties of these complexes and particularly their infrared spectra have not been studied to any extent. In this section the infrared spectra and magnetic properties will be discussed with a view to characterizing the complexes and assigning bands in the infrared

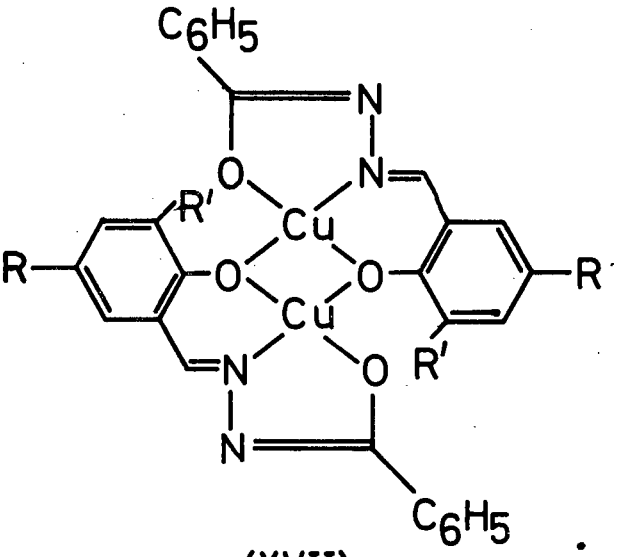
spectra in order to obtain information regarding the metal-ligand bonding. The infrared spectra are reported in Tables 41 to 44 and are shown in Figure 27 . The magnetic measurements are reported in Tables 70 to 72 .

The magnetic moments of a number of CuL(pyridine) and CuL(N-N) complexes have been reported[184,335] to lie within the normal range for one unpaired electron. The values found for the ammine complexes (Table 70) and two α-diimine complexes (Table 71) confirm this and indicate that there is no Cu-Cu interaction in these complexes. The magnetic moments for the complexes having the empirical formula CuL have been reported[184] to lie within the range 1.02 to 1.20 Bohr magnetons. The moments obtained in the present work for these complexes (Table 72) are either within this (subnormal) range or are near to the normal value for one unpaired electron. It is when a substituent is in the 3-position on the salicylidene ring that the magnetic moments do not show subnormal values.

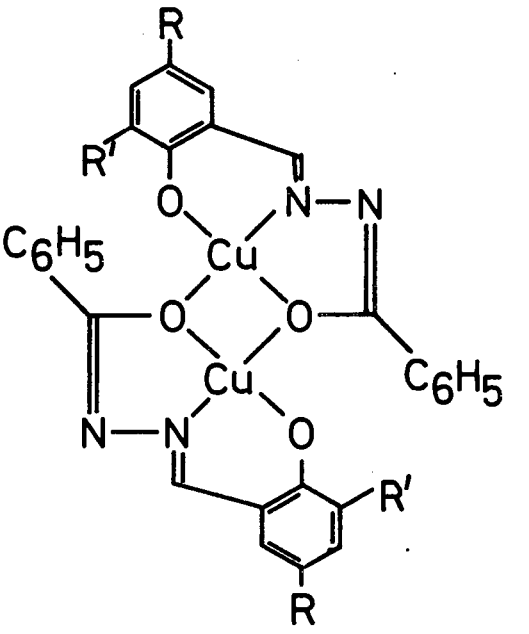
Subnormal magnetic moments for copper complexes have been widely reported[200] and have been shown to occur when the molecule is dimeric. Benzoylsalicylidenehydrazone is a typical example of a tridentate ligand which may produce dimeric molecules by means of oxygen atoms bridging two copper atoms. Two alternative symmetrical structures (XVII) and (XVIII) are possible, depending on whether the salicylidene oxygen atoms or the benzoyl oxygen atoms are those participating in the bridging. Another isomer is possible with one each of the salicylidene and benzoyl oxygen atoms being those in the bridge. The crystal structure[336] of a compound showing dimer formation, acetylacetone-mono(2-hydroxyanil) copper(II), indicates that it is the phenolic oxygen atom and not the acetyl oxygen which bridges the copper atoms. If this can be taken as



(XVI)



(XVII)



(XVIII)

a general rule, structure (XVII) will be preferred.

The two complexes with no substituents in the 3-position on the salicylidene ring exhibit definitely subnormal magnetic moments. This is in agreement with the values previously obtained[184] for similar complexes, where no substituent was present in the 3-position on the salicylidene ring. The other four complexes, each of which has a substituent in the 3-position, have magnetic moments near to the normal value for a copper(II) ion. The data indicate that in the complexes with magnetic moments near the normal range, the substituent serves to interfere with interaction between the copper atoms. Perhaps it is merely a steric effect of the substituent which causes this interference. However, in work on the magnetic behaviour of copper complexes of N-salicylidene-2-aminophenols[337,338], the magnetic moments at about 300 K of a number of complexes were in the range 1.55 to 1.60 while the moments of two complexes studied were 1.82 and 1.87 Bohr magnetons. Only one of these complexes had a substituent in the 3-position of the salicylidene ring and it was concluded[337] that, in this compound, the phenolic oxygen atom and not the salicylidene oxygen atom participates in the bridging. In the benzoylsalicylidenehydrazone complexes, if bridging by the salicylidene oxygen was prevented by steric effects, it would be expected that the benzoyl oxygen atoms would participate in bridging.

Determination of the temperature dependence of the magnetic moments between 80 K and 300 K and the investigation of the goodness of fit of the results with the Bleaney-Bowers equation[339] is necessary for a full understanding of the magnetic properties of these complexes. Absence of facilities for the determination of temperature dependence

of magnetic moments precluded further work on the magnetic properties of these complexes.

The assignment of bands in the infrared spectra of the various copper benzoylsalicylidenehydrazone complexes offers considerable difficulty in view of the complexity of the spectra, the presence of three or four different metal-ligand bonds and the fact that isotopic labelling of the compounds was not able to be accomplished. The infrared spectra are reported in Tables 41 to 44 .

The ammine adducts generally have the formula $Cu(BR\text{-}SH)(NH_3)(H_2O)$, but two of the compounds prepared differ from this composition: the 5-CH_3 substituted complex was isolated as the hemihydrate whilst the 5-Cl substituted complex had the empirical formula $Cu(BR\text{-}SH)(NH_3)_{\frac{3}{4}}(H_2O)_{\frac{1}{2}}$. Although the latter compound was prepared three times employing a large excess of ammonia, production of the compound having one ammonia molecule per copper atom was not realised. It is assumed that the ammonia molecule, being the more basic molecule, is coordinated to the copper ion rather than the water molecule, which presumably has a space-filling function.

Comparison of the spectra within each of the three types of complexes shows that in each case the 3,5-dihalogen substituted compounds show a good band for band correspondence but that this is not extended to the other complexes of the set. For this reason, the discussion will be largely confined to the 3,5-dihalogen substituted complexes, which have identical stoichiometry and are presumably isostructural.

The infrared spectra of the ammine adducts between 200 and 650 cm^{-1} are shown in Figure 27 . Two bands, in the ranges 400 to 440 cm^{-1}

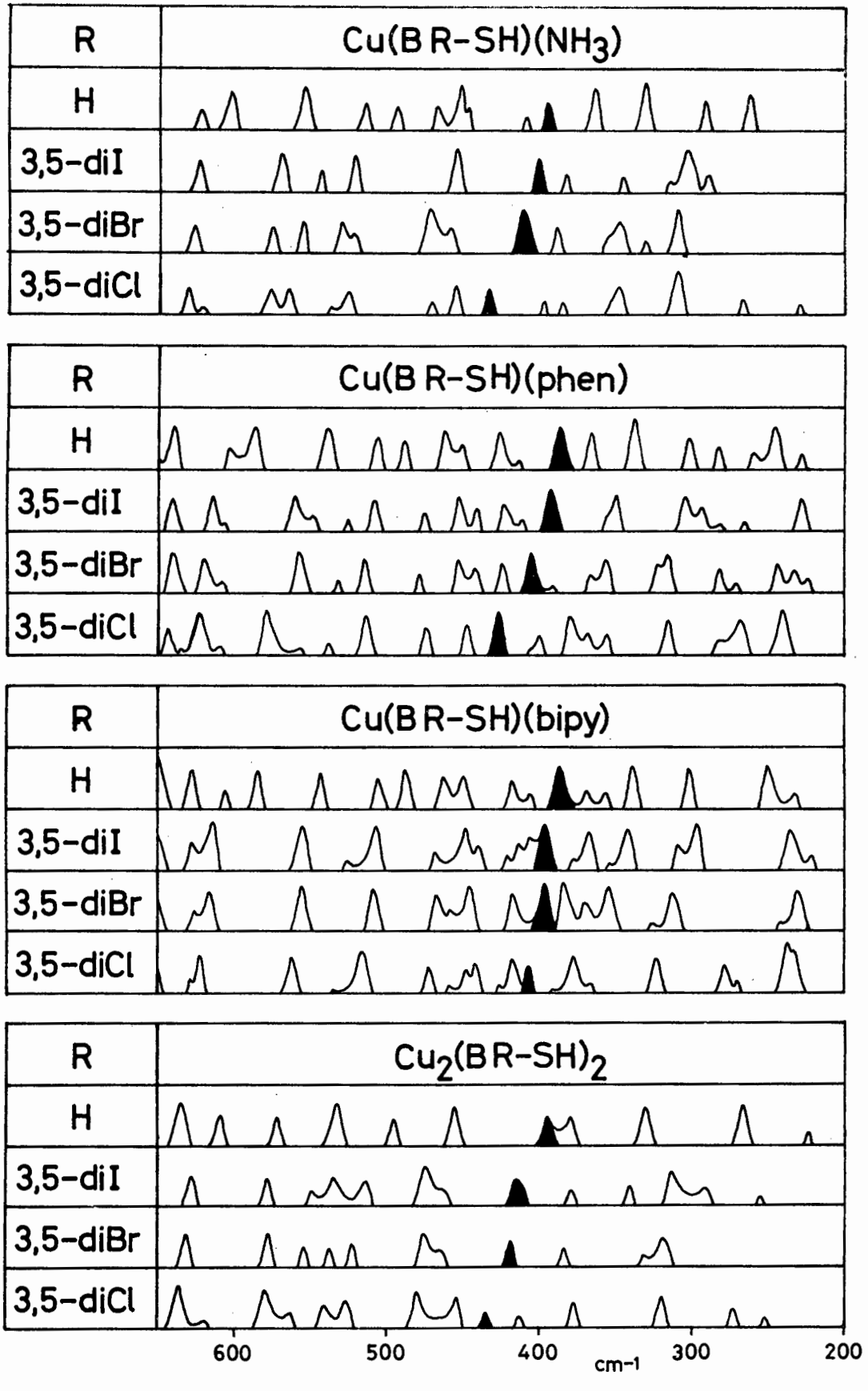


Figure 27. The infrared spectra of substituted Cu(II) benzoylsalicylidenehydrazone complexes, 200 - 650 cm^{-1}. Solid peaks : νM-N.

and 540 to 570 cm^{-1}, in the spectra of the 3,5-dihalogen substituted complexes exhibit a marked dependence on substituent, while the remaining bands below 650 cm^{-1} show very little substituent dependence. In copper N-arylsalicylaldimine complexes, Percy assigned[16] (on the basis of ^{15}N-labelling) bands in the regions 400 to 450 cm^{-1} and 490 to 510 cm^{-1} to νM-N, the lower frequency band being the vibrationally purer. Another band, showing only a small ^{15}N-sensitivity in the region 520 to 550 cm^{-1} was assigned to coupled νM-O. Furthermore, the principal νM-N showed a shift to higher frequency with increase of the combined π-electron releasing capacities of the substituents on the salicylidene ring. Taft's[22] resonance polar parameter, $\sigma_p - \sigma'$, provided a measure of these effects. The two bands selected above both show an increase in frequency with increase in magnitude of the parameter $\sigma_p - \sigma'$. In the spectrum of the unsubstituted compound, a band found in the lower frequency region correlates with the other bands both as regards frequency and value of $\sigma_p - \sigma'$ (Figure 27 and Table 80). It is suggested that this band, on account of its substituent sensitivity and similarity in frequency and behaviour to that assigned by ^{15}N-labelling, to νM-N in the N-arylsalicylaldimine complexes, be assigned to the principal νM-N, while the other band (showing less substituent sensitivity) is assigned to a more strongly coupled νM-N,

The infrared spectra of the 1,10-phenanthroline and 2,2'-bipyridine adducts between 200 and 650 cm^{-1} are shown in Figure 27 . In the spectra of the 1,10-phenanthroline adducts a band occurs in the region between 385 and 425 cm^{-1}. Its frequency is dependent on the substituent in the order H<3,5-diI<3,5-diBr<3,5-diCl. This is precisely

Table 80. νM-N in the copper benzoylsalicylidenehydrazone amine complexes Cu (BR-SH)(NH_3)(H_2O)

R	$\sigma_p - \sigma'$	νM-N
H	0.00	395
3,5-diI	-0.20	402
3,5-diBr	-0.44	410
3,5-diCl	-0.48	433

the position and substituent dependence of the band assigned to νM-N in the ammine adducts. A similar band with the same substituent sensitivity may be identified in the spectra of the 2,2'-bipyridine adducts, although the assignment is not as certain in these compounds owing to the multiplicity of bands in the region between 385 and 420 cm^{-1}. On the grounds of the similarity of its behaviour in these adducts to that in the ammine adducts and the N-arylsalicylaldimine complexes, this band is assigned to an M-N stretching vibration. Other bands below 650 cm^{-1} in the adducts do not generally show a definite substituent dependence when related to a substituent parameter of the 3,5-dihalogen substituents.

Extending this approach to the complexes having the empirical formula Cu(BR-SH) enables the assignment of M-N stretching vibrations to be made. A band is present in the spectra of these complexes in the range 495 to 535 cm^{-1} with a frequency which is substituent dependent in the order H<3,5-diI<3,5-diBr<3,5-diCl (Figure 27).

This band is assigned to νM-N and it is suggested that an additional band between 530 and 545 cm^{-1}, which has frequencies in the order H<3,5-diI< 3,5-diBr<3,5-diCl, originates in a more extensively coupled νM-N.

In the absence of isotopic labelling (unfortunately not able to be accomplished for the compounds discussed here) more conclusive assignment of νM-L is not possible. Comparison of the spectra of these complexes with those of other complexes of similar structure where ^{15}N-labelling of a donor atom was possible, permits empirical assignments of metal-nitrogen vibrations. The similar frequencies and substituent sensitivity of the assigned bands in these various sets of copper complexes and in the copper N-arylsalicylaldimine complexes[16] is a strong argument favouring the correctness of the assignment.

Extension of this approach to assignment of bands in the spectra of the 5-Cl and 3-OCH_3 substituted compounds has not been attempted. Absence of a constant stoichiometry (in the ammine adducts), the possibility of the absence of a common structure (in the Cu(BR-SH) complexes) and the effect of steric crowding by the 3-OCH_3 substituent (which produced an anomalously low frequency in the N-arylsalicylaldimine complexes[16]) renders reliable assignments difficult.

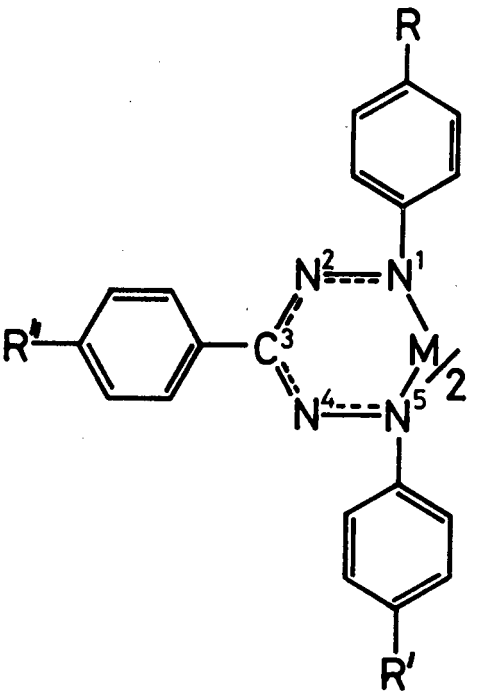
The various sets of complexes show a similar band pattern in the region between 1450 and 1650 cm^{-1}. A number of bands occur both near 1500 cm^{-1} and 1600 cm^{-1} in all the complexes. Bands in the vicinity of 1550 cm^{-1} occur in some compounds but are absent in all the 3,5-dihalogen substituted complexes. Sinn and Harris[340] have assigned a band near 1550 cm^{-1} to the stretching vibration of the C-O bond associated with a bridging oxygen atom in dimeric compounds. Absence of a band in this region in the 3,5-dihalogen substituted Cu(BR-SH) complexes could be evidence that their assignment is incorrect, if in the present case the complexes are indeed dimeric.

6. FORMAZAN COMPLEXES : THE EFFECTS OF ^{15}N-LABELLING, METAL ION SUBSTITUTION AND LIGAND SUBSTITUTION ON THEIR INFRARED SPECTRA.

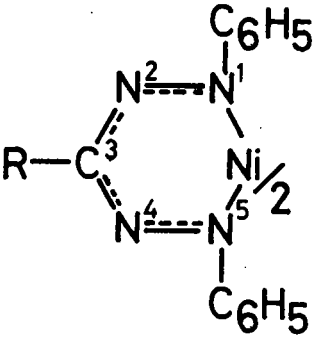
The infrared spectra of metal complexes of formazans have not received much attention. Previous work has been concerned with the assignment of ligand vibrations[220] and the differences between the infrared spectra of isomeric compounds[221]. The infrared spectra below 650 cm^{-1} of metal formazan complexes have not previously been reported.

In this section the application of ^{15}N-labelling, metal ion substitution and the effect of varying the ligand substituents to the assignment problem in the infrared spectra of complexes (XIX) and (XX) is discussed. The results enable some conclusions to be made concerning the bonding in the chelate ring and the structures of the complexes. The infrared spectra and magnetic measurements for the complexes studied are given in Tables 46 to 51 and 73, respectively.

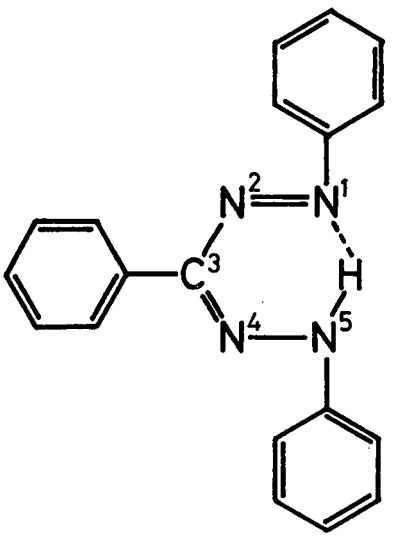
A crystal structure determination[234] of a nickel formazan complex has shown that coordination around the nickel atom is truly square planar with the ligands extensively buckled to accommodate the phenyl rings bonded to the donor atoms. The diamagnetism of nickel formazan complexes[228,231] (Table 73) confirms their general square planar coordination. The magnetic moments of only five cobalt formazan complexes have been determined[231] (Table 81). These lie within the range 1.93 to 2.24. A magnetic moment in this range is indicative of square planar or low spin octahedral coordination of a Co(II) ion[314,334]. The octahedral configuration is rendered unlikely because of the difficulty of accommodating six donor atoms around the metal ion and



(XIX)



(XX)



(XXI)

the reported failure[228] to prepare pyridine adducts of formazan complexes. It is considered that the most likely structure is the planar

Table 81. Magnetic moments of cobalt formazan complexes Co(1-R-phenyl,3,5-diphenylformazan)$_2$

R	μ(Bohr magnetons)	Reference
H	1.98 and 2.24	This work
H	1.93	4
4-F	1.95	This work
4-Cl	2.12	4
4-Br	1.97	This work
4-CH_3	2.05	4

configuration with buckled ligands which has been established for the nickel complexes.

Vibrations in the infrared spectra of triarylformazans (XXI) have been assigned empirically[220,221] and by ^{15}N-labelling[235] of the N^2 and N^4 atoms. Empirical assignments of vibrations in the spectra of some Ni(II) and Cu(II) triarylformazan complexes have been proposed[220,221] but no labelling studies on the complexes have been made nor have metal-ligand vibrations previously been assigned. The ^{15}N-labelling of the N^1 atom is employed in this work as a means of ascertaining the validity of earlier assignments of the ligand vibrations and, since the N^1 atom is coordinated to the metal ion, as a means of assigning metal-nitrogen stretching frequencies, νM-N, in the complexes.

The ^{15}N-induced shifts in the spectrum of 1,3,5-triphenylformazan are given in Table 45 and shown in Figure 28 and the assigned bands with the shifts induced by ^{15}N-labelling of the N^1 or N^2 atoms are given in Table 82 .

By analogy with salicylaldimines[15] and β-ketoenols[342] in which considerable vibrational coupling between νC=N or νC=O and νC=C occurs, it is probable that there will be extensive coupling between νC=N and νN=N in formazans and thus it is unlikely that any band can be uniquely assigned to either of these pure vibrations. However, any band which comprises a large contribution from νC=N should shift significantly on labelling the N^2 atom whilst a band predominantly comprised from νN=N should shift significantly on labelling both the N^1 and N^2 atoms. The bands which satisfy these criteria are at 1517 cm^{-1} (shifted -6 cm^{-1} on labelling N^2 and -0.3 cm^{-1} on labelling N^1) and thus predominantly νC=N and at 1237 cm^{-1} (shifted ~-12 cm^{-1} on labelling N^2 and -2.0 cm^{-1} on labelling N^1) and thus predominantly νN=N.

The labelling of the N^1 atom in contrast to the N^2 atom allows a distinction to be made between the vibrations of the C-N species within the chelate ring and those of the exocyclic C-N bond, the latter being sensitive to the labelling of the N^1 atom but not to that of the N^2 atom. The bands at 1317 and 1187 cm^{-1} are thus assigned to the exocyclic νC-N vibration. The band at 1355 cm^{-1}, being sensitive to the labelling of the N^2 atom (but not N^1) is accordingly assigned to a chelate ring νC-N vibration. The band at 1355 cm^{-1} had previously[235] been assigned to the νN=N vibration but this assignment is invalidated by its lack of sensitivity to labelling of the N^1 atom.

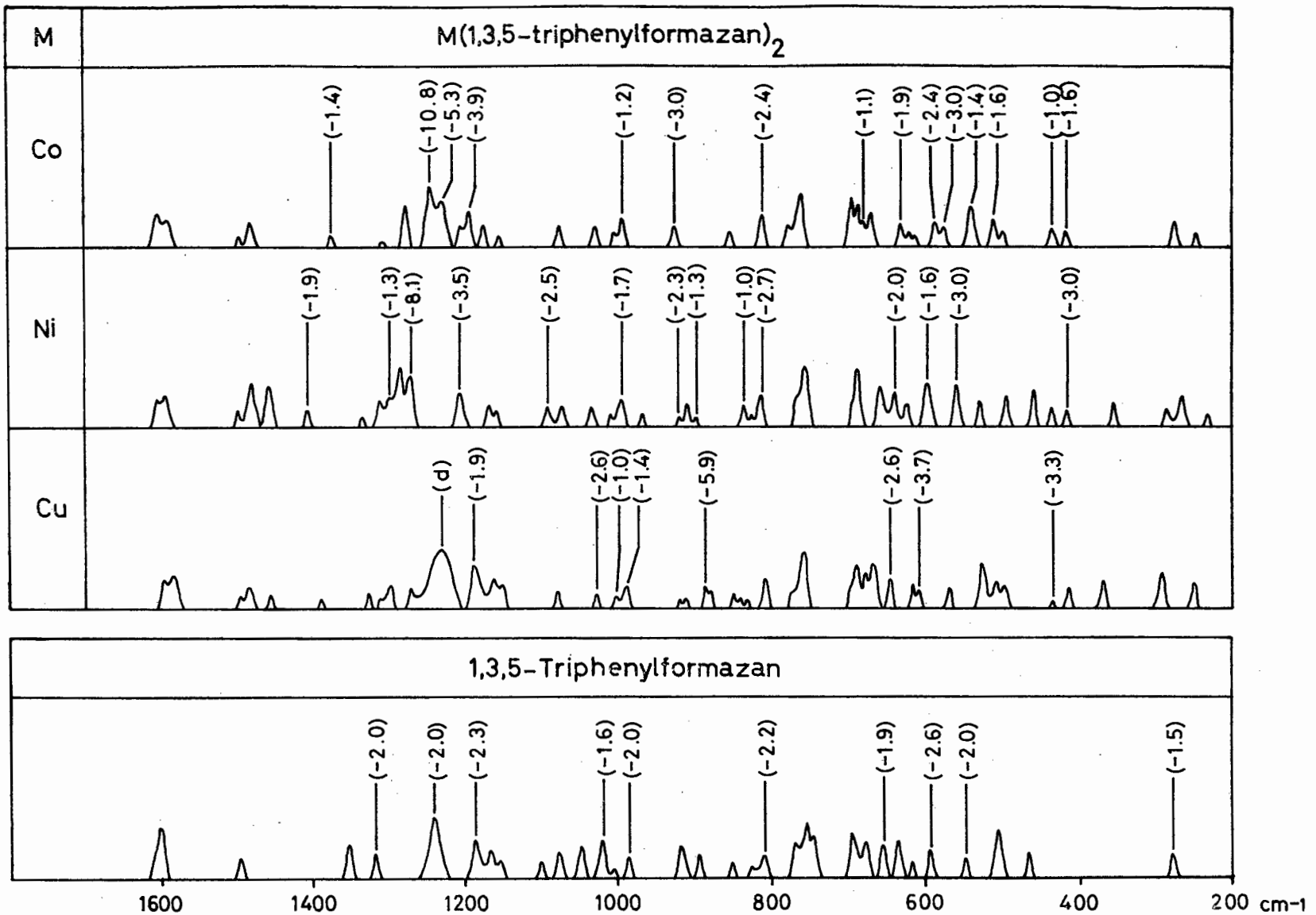


Figure 28. The infrared spectra of 1,3,5-triphenylformazan and the Co(II), Ni(II) and Cu(II) triphenylformazan complexes.

Figures in parentheses are shifts (cm^{-1}) induced by ^{15}N-labelling. For all other bands the shifts are <1.5 cm^{-1}.

Table 82: Assignments of vibrations of 1,3,5-triphenylformazan.

Frequency	Empirical assignments	^{15}N-labelled N^2 Shift	Assignment[235]	^{15}N-labelled N^1 Shift	Assignment
1603	aryl[220,221], ν(C=N)[341]			+2.4	νC=C
1517		-6	νC=N	-0.3	νC=N(+νN=N)
1509	νC=N[221], aryl[220]			-0.1	νC=N
1449	aryl[221] νN=N[220]			-0.5	νC=N
1355		~-6	νN=N	-0.5	νC-N
1317	νC-N[220,221]			-2.0	νC-N(exocyclic)
1291	νC-N[221]	not observed		not observed	
1237	νC-N[220,221]	~-12	νC-N	-2.0	νN=N(+νC=N)
1187	aryl δCH[221]			-2.3	νC-N(exocyclic)
1150	aryl δCH[221] νC-N[220]			0.0	δCH
1046	aryl δCH[220,221]	-3	νN-N	-0.9	νN-N(+νC-N)
1020	aryl δCH[220,221]	-5		-1.6	νN-N
1003	ring breathing[221]			-0.6	δCH
984	ring breathing[221]	-6	deformation	-2.0	δCNNC
918	δCNNC[221]			-0.4	δCH
806	aryl γCH[221]	-2	deformation	-2.2	δCNNC
653		-3	deformation	-1.9	δCNNC
590		-3	deformation	-2.6	δCNNC
545		-5	deformation	-2.0	δCNNC
278				-1.5	

Two bands at 1046 and 1020 cm^{-1} show sensitivity to labelling of both the N^1 and N^2 atoms and are reasonably assigned to the νN-N vibration (νN-N has been assigned[5,343] in hydrazine complexes within the region 985 to 1015 cm^{-1}). The other bands in the spectrum above 1400 cm^{-1} which show no sensitivity to ^{15}N-labelling are assigned to the νC=C vibrations associated with the phenyl rings. A number of bands between 500 and 1000 cm^{-1} show sensitivity to labelling of both the N^1 and N^2 atoms. It is proposed that they arise from deformation vibrations of the CNNC moiety. No discrete band attributable to the N-H stretching vibration is found, the absorption being diffuse between 3000 and 3600 cm^{-1}. This would indicate that this hydrogen atom is strongly hydrogen bonded to the nitrogen atom at the other end of the molecule, forming a six membered ring. A band in the region 3000 to 3100 cm^{-1} has previously been assigned to this vibration[221]. NMR results[344,345] have also indicated a high degree of hydrogen bonding in formazans.

The application of ^{15}N-labelling to the study of the infrared spectra of the triarylformazans indicates the need for revision of some assignments and enables more definite assignments to be made. In particular, the νN=N vibration which has previously been assigned in formazans to bands near 1450 cm^{-1}[220], 1355 cm^{-1}[235], 1550 cm^{-1} (in C-alkyl and C-halogen N,N'-diphenylformazans)[346], and not assigned at all in a series of detailed papers on the formazans[221,341,342] can now (by virtue of its sensitivity to the labelling of both the N^1 and N^2 atoms) be assigned to the band near 1240 cm^{-1}. The νC=N vibration has been assigned to the band near 1600 cm^{-1}[341] and to a band no higher in frequency than 1365 cm^{-1}[220]. The assignment to a band in the region

near 1515 cm^{-1}[235,221] is confirmed by the sensitivity to labelling of the N^2 atom and not the N^1 atom.

The ^{15}N-induced shifts in the spectrum of the Co(II), Ni(II) and Cu(II) 1,3,5-triphenylformazan complexes (XIX : R = R' = R'' = H) are given in Table 46 and shown in Figure 28 . The intense bands in the region 1220 - 1270 cm^{-1} are assigned to coupled νN=N. Two bands in the Co complex at 1226 ($\Delta\nu$ = -5.3) cm^{-1} and 1242 ($\Delta\nu$ = -10.8) cm^{-1} and one band in the Ni complex at 1270 ($\Delta\nu$ = -8.1) cm^{-1} are thus assigned. The bands are considerably coupled, since a ^{15}N-induced shift of -20 cm^{-1} is expected for an uncoupled N=N stretching vibration[49]. In the Cu complex a very broad band centred at 1232 cm^{-1} is split on ^{15}N-labelling into a doublet at 1231 and 1249 cm^{-1}. The ^{15}N-induced shift consequently cannot be determined but this band is nevertheless assigned to νN=N because of its similar position and intensity to the bands so assigned in the Co and Ni complexes. These assignments agree with those proposed by Arnold and Schiele[221] for variously substituted Ni complexes and by le Fevre, Sousa and Werner[220] who reported bands at 1250 and 1237 cm^{-1} for the Cu complex and assigned the higher frequency band to νN=N.

The ^{15}N-sensitive bands at 1192 ($\Delta\nu$ = -3.9), 1204 ($\Delta\nu$ = -3.5) and 1185 ($\Delta\nu$= -1.9) cm^{-1} in the Co, Ni and Cu complexes respectively, are assigned to the exocyclic νC-N. The most likely bands which can be assigned to νC=N are those in the regions 1450 to 1500 cm^{-1} and near 1600 cm^{-1}. However, none of these bands shows even a small negative shift which would result from coupling of this vibration with those

involving the ^{15}N-labelled atom, most showing small shifts to higher frequency. For this reason, the bands near 1400 cm^{-1}, which have small negative ^{15}N-induced shifts, can possibly be assigned to $\nu C{=}N$. In the absence of ^{15}N-labelling of the N^2 atom, the assignment of a band to $\nu C{=}N$ cannot be made with certainty. Previously, in the Ni complexes the intense band near 1280 cm^{-1} has been assigned[221] to the C-N stretching vibration in the chelate ring and two bands near 1300 cm^{-1} to the exocyclic $\nu C{-}N$ and in the Cu complexes bands near 1240 and 1330 cm^{-1} are assigned[220] to C-N vibrations without specifying the atoms involved in the vibration.

Most of the bands above 1450 cm^{-1} can be assigned to the stretching vibrations of the phenyl rings. None of these bands show a ^{15}N-induced shift to lower frequency. The bands near 990 cm^{-1} showing small ^{15}N-induced shifts can probably be assigned to the $\nu N{-}N$ vibration[343] and those near 800 and 900 cm^{-1} to a deformation vibration involving the CNNC moiety, $\delta CNNC$. Bands between 800 and 900 cm^{-1} have been assigned to the δCNC vibration in metal N-arylsalicylaldimine complexes[15].

Below 700 cm^{-1}, the Co(II), Ni(II) and Cu(II) complexes of triphenylformazan do not show an exact band for band correspondence in their infrared spectra (Figure 29). This feature suggests that the complexes are not structurally identical although the differences in the band patterns, particularly for the Co and Ni complexes, are not sufficiently large as to imply any gross differences in symmetry. The bands exhibiting maximum sensitivity to ^{15}N-labelling of the N^1 atom all occur within the range 550 - 620 cm^{-1} and are therefore assigned as

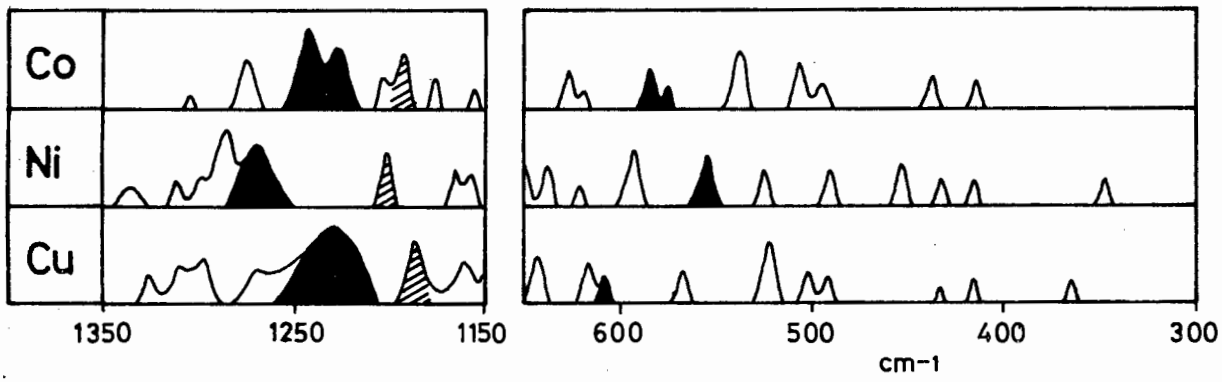


Figure 29. The effect of metal ion substitution on the infrared spectra of metal(II) triphenylformazan complexes, 300 - 650 cm^{-1} and 1150 - 1350 cm^{-1}.
Solid peaks : νM-N and νN=N; shaded peaks:exocyclic νC-N.

the principal (least-coupled) νM-N bands. They have the values : Co 574 ($\Delta\nu$ = -3.0) and 584 ($\Delta\nu$ = -2.4); Ni 553 ($\Delta\nu$ = -3.0); Cu 611 ($\Delta\nu$ = -3.7) cm^{-1} and thus their frequencies have the metal dependent order of Co>Ni<Cu.

It has been shown[8,15] that, for a pair of isostructural square planar Ni and Cu complexes, the νM-L frequencies are in the order Ni>Cu. This is the stability order expected from theoretical considerations, since the antibonding orbital of highest energy is occupied in the Cu(II) ion but is vacant in the Ni(II) ion which is spin-paired. Inclusion of the Co(II) ion in the series would give the stability order Co>Ni>Cu. Thus if the Co(II), Ni(II) and Cu(II) triphenylformazan complexes are all square planar then the order of νM-N frequencies would be Co>Ni>Cu. Crystallographic[234] and magnetic[231] (Table 81) evidence indicates that the Co and Ni complexes are square planar. Experimental evidence for the structure of the Cu complexes is lacking but they would reasonably be expected to be square planar.

The observed order of Co>Ni<Cu for the frequencies showing the highest ^{15}N-sensitivity implies that the Co and Ni complexes are essentially isostructural but that the structure of the Cu complex differs sufficiently that the expected order of frequencies is deranged. The difference may be either that the chelate ring is less severely buckled in the Cu complex than in the Ni complex, allowing increased π-bonding and thus a higher frequency or that the phenyl groups in the Cu complex are accommodated by some other structural feature such as distortion towards tetrahedral symmetry. The latter explanation seems less likely in that the Co complex does not adopt a tetrahedral configuration (which would seem more likely to reduce interaction of the

of the phenyl rings than a square planar configuration) and synthesis of Zn(II) triarylformazan complexes has not proved possible. The uncertainty in the structure of the Cu complex remains to be resolved by crystallographic studies.

Other bands in the spectra below 700 cm^{-1}, in the ranges 410 to 440 cm^{-1} and 590 to 645 cm^{-1}, can be assigned to more highly coupled νM-N vibrations. These bands show smaller ^{15}N- and metal-sensitivities than the principal νM-N band.

Bands assigned on the basis of their ^{15}N-sensitivities to νN=N and the exocyclic νC-N exhibit metal ion dependence in the order Co<Ni>Cu (Figure 29). That this order is the opposite of the order of the metal sensitivity of νM-N implies that stabilization of the M-N bonds is accomplished at the expense of the adjacent N=N and C-N bonds.

It has frequently been found that the metal-ligand stretching frequencies in metal complexes are shifted by substitution in the ligand. Good correlations have been found between the electronic effects of substituents and νM-L in metal N-aryl- and N-alkyl-salicylaldimine complexes[15,16,17], metal anthranilate complexes[12], and nitrobis(acetylacetonato)aniline cobalt(III) complexes[37].

In the triarylformazan complexes substitution is possible on the aryl ring bound to the N^1 (or N^5) atoms, on both the aryl rings bound to the N^1 and N^5 atoms or on the aryl ring bound to the C atom. The infrared spectra of the Ni complexes substituted in the 4-position of the aryl rings are given in Tables 47 to 49 and the regions between 200 and 650 cm^{-1} are shown in Figures 30 to 32 .

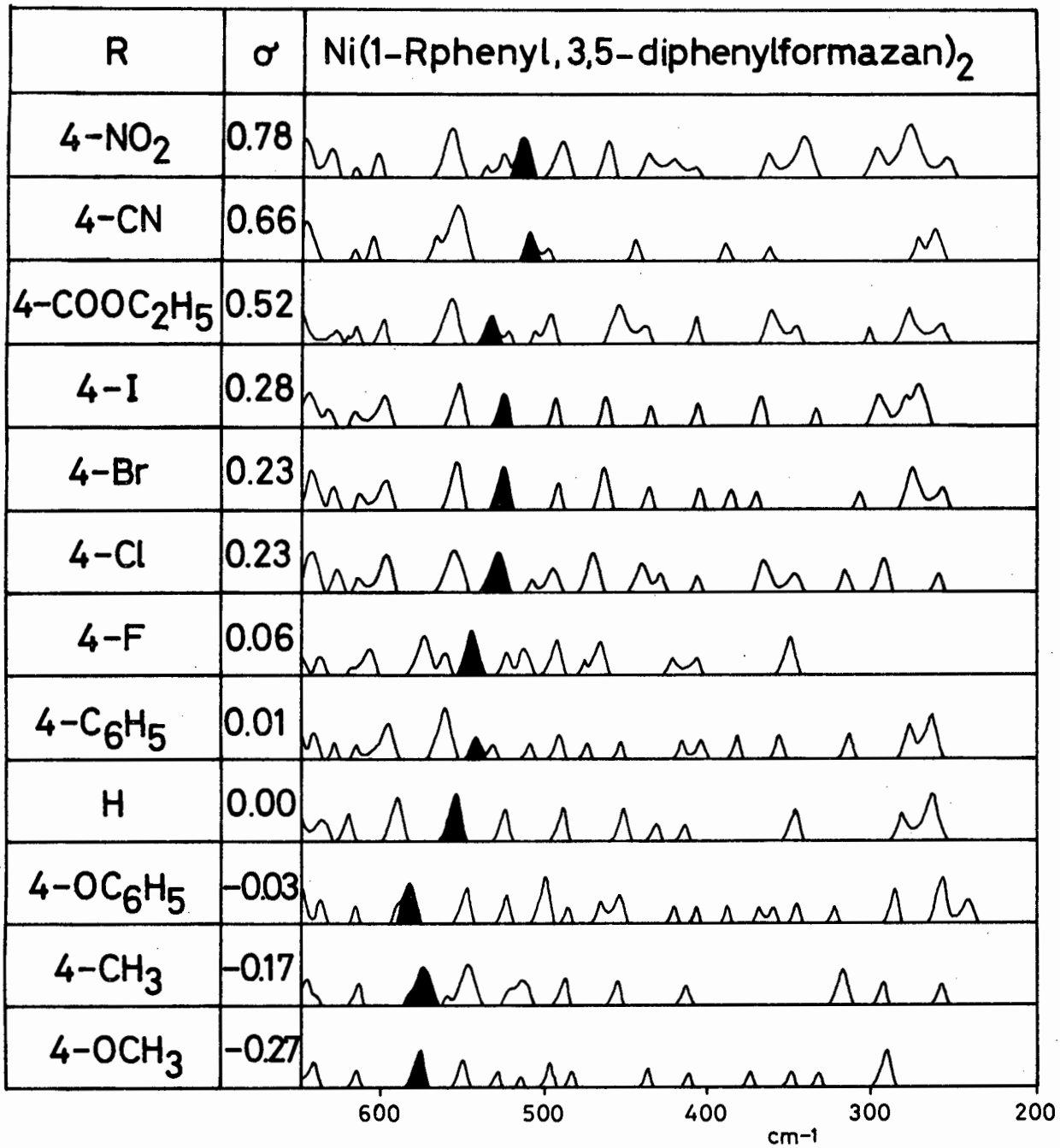


Figure 30. The infrared spectra of substituted Ni(II) triarylformazan complexes, 200 - 650 cm^{-1}. Solid peaks : νM-N.

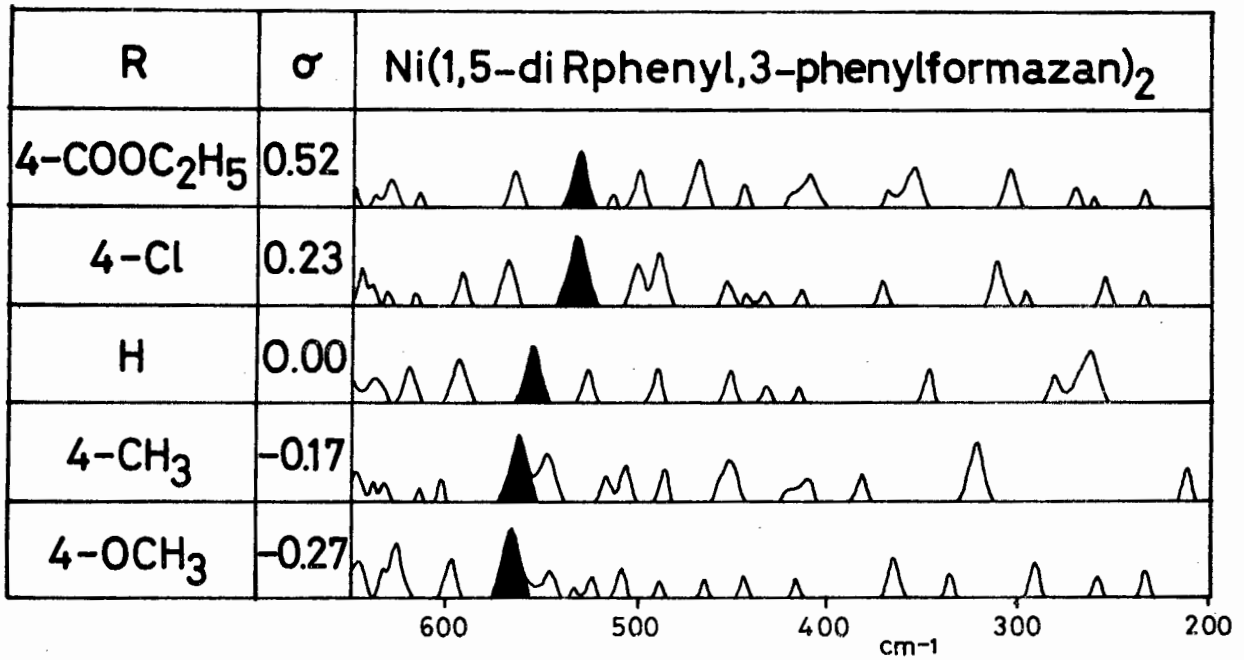


Figure 31. The infrared spectra of substituted Ni(II) triarylformazan complexes, 200 - 650 cm^{-1}. Solid peaks : νM-N.

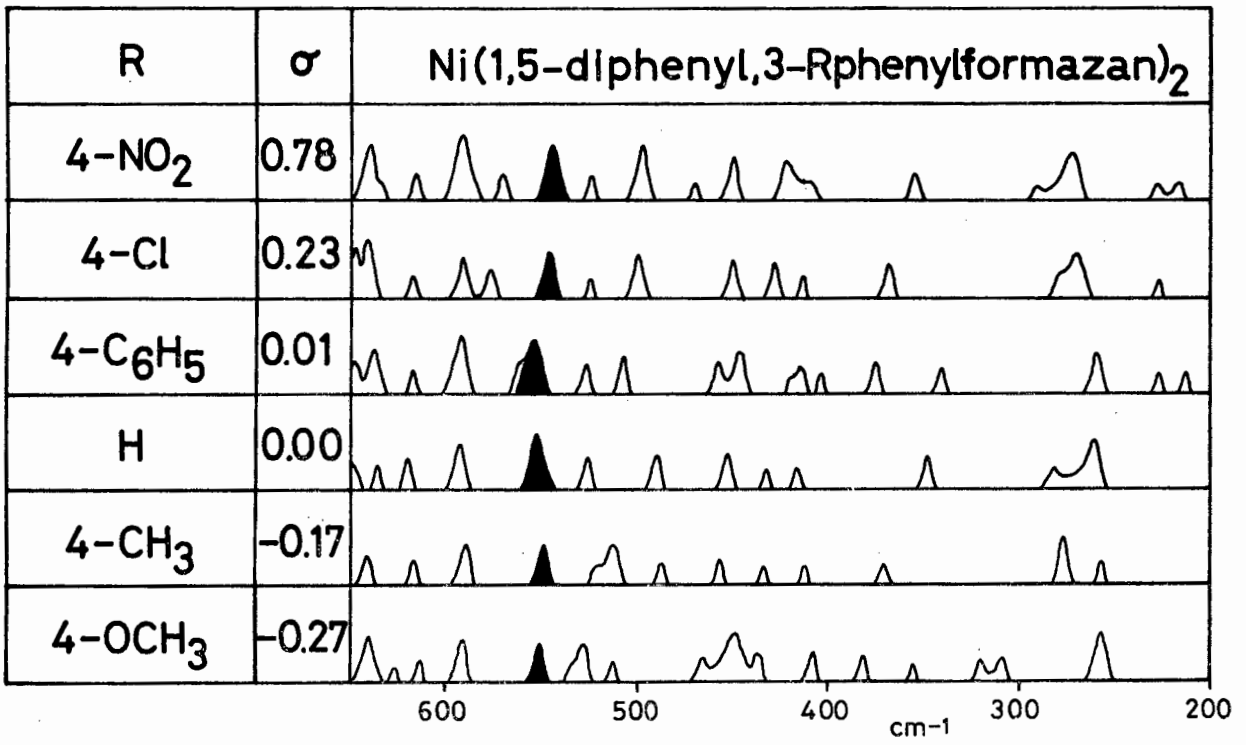


Figure 32. The infrared spectra of substituted Ni(II) triarylformazan complexes, 200 - 650 cm^{-1}. Solid peaks : νM-N

In those cases where the substituents are on the aryl rings bound to nitrogen atoms the band which has been assigned to the principal νM-N on the grounds of its ^{15}N-sensitivity is found to be shifted to lower frequency by electron withdrawing substituents and to higher frequency by electron releasing substituents (Figures 30 and 31). However, when the substituent is on the aryl ring bound to the carbon atom, this band is not shifted significantly by either electron withdrawing or electron releasing substituents (Figure 32). This result is reasonable in that the M-N bond order would be expected to be more affected by substituents on N^1- or N^5- aryl rings than by substituents on the C-aryl ring.

Of the substituted Co complexes only two (XIX; M = Co, R'=R''=H, R=4-F or 4-Br) could be synthesized in an analytically pure state. Their spectra and those of the corresponding Ni complexes are given in Table 50 . Figure 33 shows these spectra below 650 cm^{-1} and between 1150 and 1350 cm^{-1}.

It is seen that in each set of complexes, corresponding bands can be identified which in the substituted complexes show the same behaviour as those bands assigned, on account of their ^{15}N-sensitivity, to νM-N, νN=N and νC-N in the unsubstituted complexes (Figures 28 and 29). Further, the band assigned to νM-N shows the same substituent sensitivity in the Co complexes as in the Ni complexes. This evidence supports the isostructural character of the Co and Ni complexes and further validates the proposed assignment of the principal νM-N in these complexes.

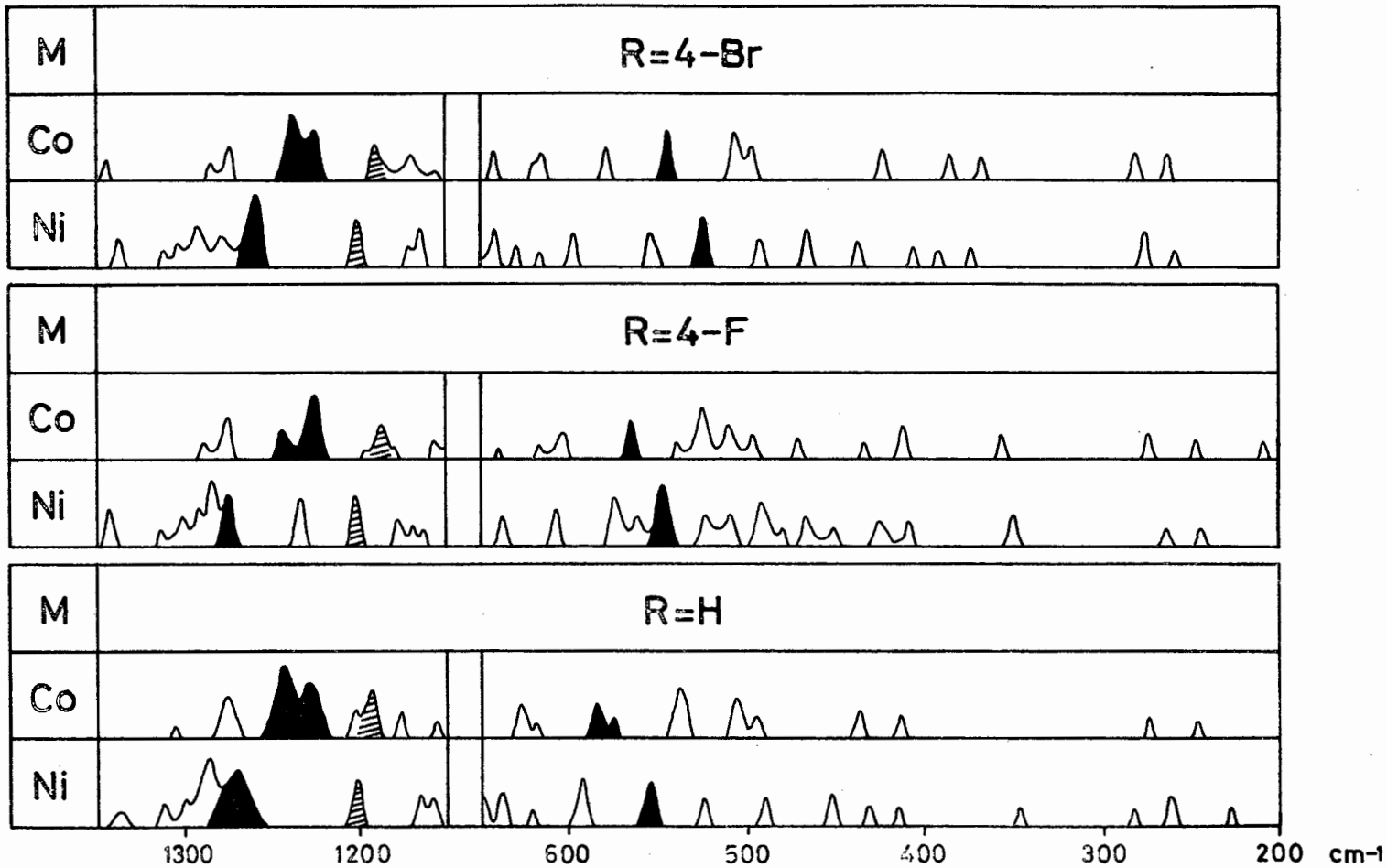


Figure 33. The effect of metal ion substitution on the infrared spectra of metal(II) triarylformazan complexes, 200 - 650 cm^{-1} and 1150 - 1350 cm^{-1}. Solid peaks : νM-N and νN=N. Shaded peaks : exocyclic νC-N.

In contrast to the complexes of triarylformazans, complexes can also be prepared where a substituent is bonded directly to the chelate ring. The infrared spectra of the nickel complexes of 3-substituted-1,5-diphenylformazans (XX) are given in Table 51 and the regions between 200 and 650 cm^{-1} and 1230 and 1380 cm^{-1} are shown in Figure 34 .

Examination of the spectra shows a pronounced shift in the intense bands near 1300 cm^{-1}, one of which has been assigned to νN=N in the 1,3,5-triarylformazan complexes. It is observed that the frequencies are generally shifted to higher frequency with increased electron withdrawal by a resonance mechanism, Swain and Lupton's[27] resonance parameter *R* providing a measure of this effect (Table 83).

The shift produced is a very striking feature of the spectra and indicates that direct conjugation of the substituent with the chelate ring results in a pronounced change in the bond order of the N=N bond.

Table 83. νN=N and νM-N for the nickel 3-substituted-1,5-diphenylformazan complexes.

3-substituent	*R*	νN=N	νM-N	
CN	0.18	1349, 1321	494	458
$COOC_2H_5$	0.14	1339, 1320	535	475
$COCH_3$	0.20	1341, 1306	550	506
H	0.00	1318	552	530
NO_2	0.16	1281	573	535
CH_3	-0.14	1267	582	543
C_6H_5	-0.09	1280	592	553

It is possible that the increase in bond order with the electron withdrawing properties of the substituents may be related to increased

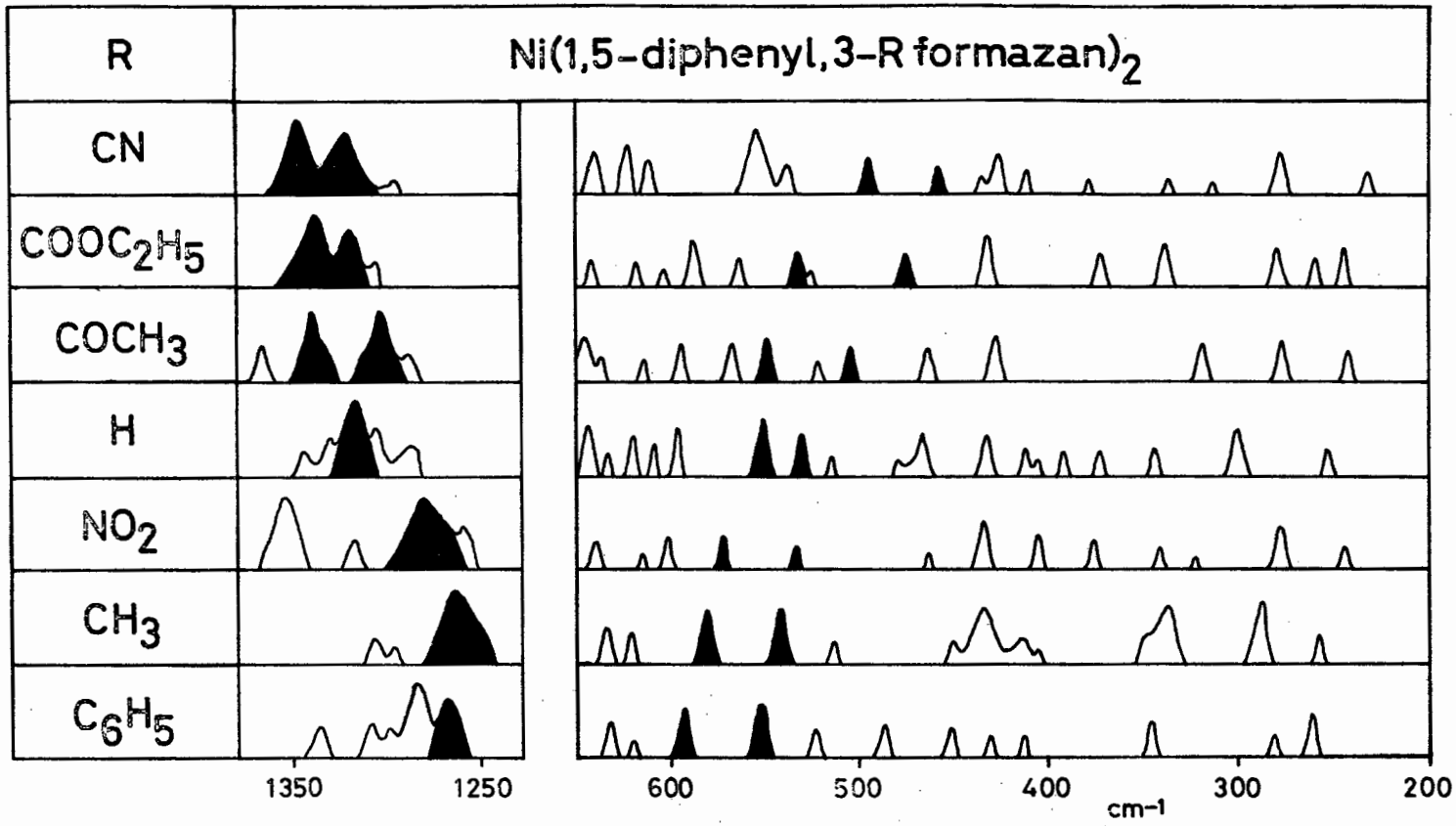


Figure 34. The infrared spectra of 3-substituted Ni(II) 1,5-diphenylformazan complexes, 200 - 600 cm^{-1} and 1230 - 1380 cm^{-1}.
Solid peaks : νM-N and νN=N.

delocalization of electrons in the chelate ring. No ready explanation can be found for the anomalous position of the bands in the NO_2-substituted complex (the band at 1357 cm^{-1} is not assigned to νN=N since absorption from the symmetric NO_2 stretching vibration is expected[349] in this region).

Two bands between 550 and 600 cm^{-1} are assigned (by ^{15}N-labelling) to νM-N in the spectrum of the nickel 1,3,5-triphenylformazan complex. Two analogous bands may be identified in the spectra of this set of complexes (Figure 34 and Table 83), which are shifted to lower frequency with increased electron withdrawal by a resonance mechanism. This is a shift in the opposite direction to that which occurs in νN=N and it is therefore concluded that in these complexes, destabilization of the M-N bonds results from electron withdrawal, and this may partly account for the stabilization of the N=N bonds. Definite assignments of νM-N in these complexes must await more complete isotopic labelling studies.

V. REFERENCES

1. B.N.FIGGIS, *Introduction to Ligand Fields, Interscience, New York*, (1966) p.244.
2. C.K.JORGENSEN, *Absorption Spectra and Chemical Bonding in Complexes, Pergamon, London*, (1962) p.110.
3. P.GEORGE and D.S.McCLURE, *Progr.Inorg.Chem.*, 1(1959) 381.
4. L.SACCONI and A.SABATINI, *Nature*, 186 (1960) 549.
5. L.SACCONI and A.SABATINI, *J.Inorg.Nucl.Chem.*, 25 (1963) 1389.
6. R.D.HANCOCK and D.A.THORNTON, *J.Mol.Structure*, 4 (1969) 361.
7. G.C.PERCY and D.A.THORNTON, *J.Mol.Structure*, 10 (1971) 39.
8. R.D.HANCOCK and D.A.THORNTON, *J.S.Af. Chem. Inst.*, 23 (1970) 71.
9. L.G.HULETT and D.A.THORNTON, *Spectrochim.Acta*, 27A (1971) 2089.
10. G.S.SHEPHARD and D.A.THORNTON, *Helv.Chim.Acta*, 54 (1971) 2212.
11. R.D.HANCOCK and D.A.THORNTON, *J.Mol.Structure*, 6 (1970) 441.
12. G.S.SHEPHARD and D.A.THORNTON, *J.Mol.Structure*, 16 (1973) 321.
13. L.G.HULETT and D.A.THORNTON, *J.Mol.Structure*, 13 (1972) 115.
14. L.G.HULETT and D.A.THORNTON, *Chimia*, 26 (1972) 72.
15. G.C.PERCY and D.A.THORNTON, *J.Inorg.Nucl.Chem.*, 34 (1972) 3357.
16. G.C.PERCY and D.A.THORNTON, *J.Inorg.Nucl.Chem.*, 35 (1972) 2319.
17. G.C.PERCY and D.A.THORNTON, *J.Inorg.Nucl.Chem.*, 34 (1973) 3369.
18. P.R.WELLS, *Chem.Revs.*, 63 (1963) 171.
19. L.P.HAMMETT, *Physical Organic Chemistry, McGraw-Hill, New York*, (1940) p.184.
20. H.H.JAFFE, *Chem.Revs.*, 53 (1953) 191.
21. D.H.McDANIEL and H.C.BROWN, *J.Org.Chem.*, 23 (1958) 420.
22. R.W.TAFT, in M.S.NEWMAN (editor), *Steric Effects in Organic Chemistry, Wiley, New York* (1956).
23. R.W.TAFT, *J.Amer.Chem.Soc.*, 75 (1953) 4231.
24. J.D.ROBERTS and W.T.MORELAND, *J.Amer.Chem.Soc.*, 75 (1953) 2167.
25. R.W.TAFT and I.C.LEWIS, *J.Amer.Chem.Soc.*, 80 (1958) 2436.
26. M.J.S.DEWAR and P.J.GRISDALE, *J.Amer.Chem.Soc.*, 84 (1962) 3539, 3548.
27. C.G.SWAIN and E.C.LUPTON, *J.Amer.Chem.Soc.*, 90 (1968) 4328.
28. P.J.KRUEGER and H.W.THOMPSON, *Proc.Roy.Soc.*, 234A (1957) 143.
29. P.J.KRUEGER and D.W.SMITH, *Canad.J.Chem.*, 45 (1967) 1605.
30. P.J.STONE and H.W.THOMPSON, *Spectrochim. Acta*, 10 (1957) 17.
31. H.W.THOMPSON and D.A.JAMESON, *Spectrochim. Acta*, 13 (1958) 236.

32. J.M.HAIGH, N.P.SLABBERT and D.A.THORNTON, *J.Mol.Structure*, 7 (1971) 199.

33. J.M.HAIGH, N.P.SLABBERT and D.A.THORNTON, *J.Inorg.Nucl.Chem.*, 32 (1970) 3635.

34. J.M.HAIGH and D.A.THORNTON, *J.Inorg.Nucl.Chem.*, 33 (1971) 1787.

35. J.M.HAIGH and D.A.THORNTON, *J.Mol.Structure*, 8 (1971) 351.

36. G.S.SHEPHARD, *Ph.D. Thesis, University of Cape Town*, (1973).

37. C.A.FLEMING and D.A.THORNTON, *Spectros.Lett.*, 6 (1973) 245.

38. C.A.FLEMING, *Ph.D Thesis, University of Cape Town*, (1973).

39. K.NAKAMOTO, *Instrument News*, 20 (1970) 1.

40. K.NAKAMOTO and A.E.MARTELL, *J.Chem.Phys.*, 32 (1960) 588.

41. K.NAKAMOTO, P.J.McCARTHY, A.RUBY and A.E.MARTELL, *J.Amer. Chem.Soc.*, 83 (1961) 1066.

42. K.NAKAMOTO, Y.MORIMOTO and A.E.MARTELL, *J.Phys.Chem.*, 66 (1962) 346.

43. M.MIKAMI, I.NAKAGAWA and T.SHIMANOUCHI, *Spectrochim.Acta*, 23A (1967) 1037.

44. G.T.BEHNKE and K.NAKAMOTO, *Inorg.Chem.*, 6 (1967) 433.

45. J.S.STRUKL and J.L.WALTER, *Spectrochim.Acta*, 27A (1971) 223.

46. K.NAKAMOTO, *Infrared Spectra of Inorganic and Coordination Compounds, 2nd Edn., Wiley-Interscience, New York*, (1970).

47. M.GOLDSTEIN, E.F.MOONEY, A.ANDERSON and H.A.GEBBIE, *Spectrochim.Acta*, 21 (1965) 105.

48. R.D.HANCOCK and D.A.THORNTON, *J.Mol.Structure*, 4 (1969) 377.

49. S.PINCHAS with I.LAULICHT, *Infrared Spectra of Labelled Compounds, Academic Press, London*, (1971).

50. E.P.DUDEK and G.DUDEK, *Inorg.Nucl.Chem.Lett.*, 3 (1967) 241.

51. H.MUSSO and H.JUNGE, *Tet.Lett.*, (1966) 4003.

52. H.JUNGE and H.MUSSO, *Spectrochim.Acta*, 24A (1968) 1219.

53. S.PINCHAS, B.L.SILVER and I.LAULICHT, *J.Chem.Phys.*, 46 (1967) 1056.

54. H.JUNGE, *Spectrochim.Acta*, 24A (1968) 1957.

55. M.J.CLEARE and W.P.GRIFFITH, *J.Chem.Soc.A*, (1967) 1144.

56. E.MIKI, *Bull.Chem.Soc.Japan*, 41 (1968) 1835.

57. B.HUTCHINSON, J.TAKEMOTO and K.NAKAMOTO, *J.Amer.Chem.Soc.*, 92 (1970) 3335.

58. K.NAKAMOTO, C.UDOVICH and J.TAKEMOTO, *J.Amer.Chem.Soc.*, 92 (1970) 3973.

59. K.NAKAMOTO, K.SHOBATAKE and B.HUTCHINSON, *Chem.Comm.*, (1969) 1451.

204. R.M.ISSA, M.F.EL-SHAZLY and M.F.ISKANDER, *Z.Anorg.Allg.Chem.*, 354 (1967) 90.

205. L.EL SAYED and M.F.ISKANDER, *J.Inorg.Nucl.Chem.*, 39 (1971) 435.

206. H.OHTA, *Chem.Soc.Jap.Bull.*, 33 (1960) 1337.

207. R.M.ISSA, M.F.ISKANDER and M.F.EL-SHAZLY, *Z.Anorg.Allg.Chem.*, 354 (1967) 98.

208. I.M.ISSA, R.M.ISSA, Y.M.TEMERK and M.M.GHONEIM, *Monatsh.Chem.*, 104 (1973) 963.

209. L.SACCONI, *J.Amer.Chem.Soc.*, 74 (1952) 4503.

210. L.SACCONI, *J.Amer.Chem.Soc.*, 76 (1954) 3400.

211. L.SACCONI, *J.Amer.Chem.Soc.*, 79 (1957) 4067.

212. H.OHTA, *Chem.Soc.Jap.Bull.*, 31 (1958) 1056.

213. H.OHTA, *Chem.Soc.Jap.Bull.*, 33 (1960) 202.

214. K.K.NARANG and A.AGGARWAL, *Inorg.Chim.Acta*, 9 (1974) 137.

215. R.L.DUTTA and G.P.SEN GUPTA, *J.Indian Chem. Soc.*, 50 (1973) 640.

216. W.D.HOOPER, *Rev. Pure Appl.Chem.* 19 (1969) 221.

217. H.VON PECHMANN, *Ber.*, 25 (1892) 3175.

218. E.BAMBERGER and E.WHEELWRIGHT, *Ber.*, 25 (1892) 3201.

219. L.HUNTER and C.B.ROBERTS, *J.Chem.Soc.*, (1941) 820, 823.

220. R.J.W.LE FEVRE, J.B.SOUSA and R.L.WERNER, *Aust.J.Chem.*, 9 (1956) 161.

221. G.ARNOLD and C.SCHIELE, *Spectrochim.Acta*, 25A (1969) 685, 697.

222. T.A.LISS and D.R.BAER, *Inorg.Chem.*, 8 (1969) 1328.

223. I.I.KUKUSHKINA, E.N.YURCHENKO, D.K.ARKHIPENKO and B.A.OREKHOV, *Zh.Fiz.Khim.*, 46 (1972) 1677.

224. E.N.YURCHENKO, I.I.KUKUSHKINA, M.I.ERMAKOVA and N.I.LATOSH, *Tr.Ural.Politekh.Inst.*, (1970) No. 190, 14.

225. R.WIZINGER and H.HERZOG, *Helv.Chim.Acta*, 36 (1953) 531.

226. B.HIRSCH, *Ann.*, 637 (1960) 167, 173, 189.

227. B.HIRSCH and E.A.JAUER, *Ann.*, 682 (1965) 99.

228. H.IRVING, J.B.GILL and W.R.CROSS, *J.Chem.Soc.*, (1960) 2087.

229. F.BEFFA, P.LIENHARD, E.STEINER and G.SCHETTY, *Helv.Chim. Acta*, 46 (1963) 1369.

230. R.PRICE, *J.Chem.Soc. A*, (1971) 3379, 3385.

231. M.I.ERMAKOVA, E.I.KRYLOV and I.Y.POSTOVSKII, *Zh.Obshchei Khim.*, 30 (1960) 849.

232. B.W.BUDESINSKY and J.SVEC, *Inorg.Chem.*, 10 (1971) 313.

233. I.I.ELBEIH, A.S.SHAWALI and M.A.ABOTABL, *Fresenius' Z. Anal.Chem.*, 261 (1972) 124.

234. D.DALE, *J.Chem.Soc.A*, (1967) 278.

235. W.OTTING and F.A.NEUGEBAUER, *Ber.*, 102 (1969) 2520.

236. R.L.BRAUN and E.C.LINGAFELTER, *Acta Cryst.*, 21 (1966) 546.

237. B.N.FIGGIS and J.LEWIS, *Progr.Inorg.Chem.*, 6 (1964) 37.

238. K.R.KOPECKY, D.NONHEBEL, G.MORRIS and G.S.HAMMOND, *J.Org.Chem.*, 27 (1962) 1036.

239. C.J.KIBLER and A.WEISSBERGER, *Org.Synth.*, 25 (1945) 7.

240. W.C.FERNELIUS and B.E.BRYANT, *Inorg.Synth.*, 5 (1957) 105.

241. E.W.BERG and J.T.TRUEMPER, *J.Phys.Chem.*, 64 (1960) 487.

242. F.A.COTTON and J.P.FACKLER, *J.Amer.Chem.Soc.*, 83 (1961) 2818.

243. J.A.BERTRAND and R.I.KAPLAN, *Inorg.Chem.*, 5 (1966) 489.

244. F.GOGAN, A.E.O'BRIAIN, E.M.PHILBIN, N.S.O'CONNOR, R.F.TIMONEY and T.S.WHEELER, *Tet.*, 3 (1958) 140.

245. R.H.HOLM and F.A.COTTON. *J.Amer.Chem.Soc.*, 80 (1958) 5658.

246. R.A.MORTON and W.C.V.ROSNEY, *J.Chem.Soc.*, (1926) 707.

247. R.A.MORTON, A.HASSAN and T.C.CALLOWAY, *J.Chem.Soc.*, (1934) 883.

248. R.N.HASZELDINE, W.K.R.MUSGRAVE, F.SMITH and L.M.TURTON, *J.Chem.Soc.*, (1951) 609.

249. G.S.HAMMOND, W.G.BORDUIN and G.A.GUTER, *J.Amer.Chem.Soc.*, 81 (1959) 4682.

250. H.E.ZAUGG and A.D.SCHAEFER, *J.Amer.Chem.Soc.*, 87 (1965) 1857.

251. D.C.NONHEBEL, *J.Chem.Soc.C*, (1968) 676.

252. H.E.ACLY and H.S.FRENCH, *J.Amer.Chem.Soc.*, 49 (1927) 847.

253. P.R.SINGH and R.SAHAI, *Inorg.Chim.Acta*, 2 (1968) 102.

254. A.G.MUFTAKOV, V.A.ALEKSEEVSKII and R.K.RAKHIMOV, *Uzb.Khim. Zh.* 15 (1971) 28.

255. D.OGDEN and J.SELBIN, *J.Inorg.Nucl.Chem.*, 30 (1968) 1227.

256. G.STRUVE, *J.Prakt.Chem.*, 50 (1894) 295.

257. J.N.ASHLEY, B.M.DAVIS, A.W.NINEHAM, R.SLACK, *J.Chem.Soc.*, (1953) 3881.

258. D.M.HUBBARD and E.W.SCOTT, *J.Amer.Chem.Soc.*, 65 (1943) 2390.

259. H.IRVING and R.J.P.WILLIAMS, *J.Chem.Soc.*, (1953) 3192.

260. D.M.ADAMS, *Metal-ligand and Related Vibrations, Arnold, London*, (1967).

261. J.R.FERRARO, *Low-frequency Vibrations of Inorganic and Coordination Compounds, Plenum Press, New York*, (1971).

262. K.H.SCHMIDT and A.MULLER, *J.Mol.Structure*, 22 (1974) 343.

263. G.F.SVATOS, D.M.SWEENEY, S.MIZUSHIMA, C.CURRAN and J.V.QUAGLIANO, *J.Amer.Chem.Soc.*, 79 (1957) 3313.

264. L.S.FORSTER, *J.Amer.Chem.Soc.*, 86 (1964) 3001.

265. N.V.SIDGWICK and F.M.BREWER, *J. Chem.Soc.*, 127 (1925) 2379.

266. A.H.MAKI and B.R.McGARVEY, *J.Chem.Phys.*, 29 (1958) 31.

267. T.S.PIPER and R.L.BELFORD, *Mol.Phys.*, 5 (1962) 169.

268. E.S.STERN and C.J.TIMMONS, *Electronic Absorption Spectroscopy in Organic Chemistry, Second edition, Arnold, London,* (1970) p.113.

269. D.OGDEN and J.SELBIN, *J.Inorg.Nucl.Chem.*, 30 (1968) 1227.

270. C.A.FLEMING and D.A.THORNTON, *J.Mol.Structure*, 25 (1974) 271.

271. R.D.HANCOCK and D.A.THORNTON, *Theor.Chim. Acta*, 18 (1970) 67.

272. P.PHEIFFER and H.GLASER, *J.Prakt.Chem.*, 151 (1938) 134.

273. P.PHEIFFER and H.GLASER, *J.Prakt.Chem.*, 153 (1939) 265.

274. T.N.WATERS and D.HALL, *J.Chem.Soc.*, (1959) 1200.

275. T.N.WATERS and D.HALL, *J.Chem.Soc.*, (1959) 1203.

276. F.J.LLEWELLYN and T.N.WATERS, *J.Chem.Soc.*, (1960) 2639.

277. D.HALL and T.N.WATERS, *J.Chem.Soc.*, (1960) 2644.

278. D.HALL, A.D.RAE and T.N.WATERS, *J.Chem.Soc.*, (1963) 5897.

279. J.M.WATERS and T.N.WATERS, *J.Chem.Soc.*, (1964) 2489.

280. A.J.McKINNON, T.N.WATERS and D.HALL, *J.Chem.Soc.*, (1964) 3290.

281. D.HALL, A.J.McKINNON and T.N.WATERS, *J.Chem.Soc.*, (1965) 425.

282. D.HALL, H.J.MORGAN and T.N.WATERS, *J.Chem.Soc.A*, (1966) 677.

283. E.N.BAKER, D.HALL and T.N.WATERS, *J.Chem.Soc.A*, (1966) 680.

284. T.P.CHEESMAN, D.HALL and T.N.WATERS, *J.Chem.Soc.A*, (1966) 685.

285. T.P.CHEESMAN, D.HALL and T.N.WATERS, *J.Chem.Soc.A*, (1966) 1396.

286. E.N.BAKER, G.R.CLARK, D.HALL and T.N.WATERS, *J.Chem.Soc.A*, (1967) 251.

287. R.D.BALL, D.HALL, C.E.F.RICKARD and T.N.WATERS, *J.Chem.Soc.A*, (1967) 1435.

288. G.R.CLARK, D.HALL and T.N.WATERS, *J.Chem.Soc.A*, (1968) 223.

289. D.HALL, S.V.SHEAT and T.N.WATERS, *J.Chem.Soc.A*, (1968) 460.

290. D.HALL, S.V.SHEAT-RUMBALL and T.N.WATERS, *J.Chem.Soc.A*, (1968) 2721.

291. D.HALL, R.H.SUMNER and T.N.WATERS, *J.Chem.Soc.A*, (1969) 420.

292. G.R.CLARK, D.HALL and T.N.WATERS, *J.Chem.Soc.A*, (1969) 2808.

293. C.A.BEAR, J.M.WATERS and T.N.WATERS, *J.Chem.Soc.A*, (1970) 2494.

294. A.W.KING, D.A.SWANN and T.N.WATERS, *J.Chem.Soc.Dalton*, (1973) 1819.

295. G.R.CLARK, D.HALL and T.N.WATERS, *J.Chem.Soc.A*, (1969) 823.

296. E.N.BAKER, D.HALL and T.N.WATERS, *J.Chem.Soc.A*, (1970) 396.

297. E.N.BAKER, D.HALL and T.N.WATERS, *J.Chem.Soc.A*, (1970) 400.

298. E.N.BAKER, D.HALL and T.N.WATERS, *J.Chem.Soc.A*, (1970) 406.

299. D.HALL, T.N.WATERS and P.E.WRIGHT, *J.Chem.Soc. Dalton*, (1973) 1508.

300. D.W.MARTIN and T.N.WATERS, *J.Chem.Soc. Dalton*, (1973) 2440.

301. J.M.STEWART and E.C.LINGAFELTER, *Acta Cryst.*, 12 (1959) 842.

302. H.C.FREEMAN, *The Biochemistry of Copper, Editors, J.Peisach, P.Aisen and W.E.Blumberg, Academic Press, New York*, (1966) p.104.

303. T.TANAKA, *Bull.Chem.Soc. Japan*, 29 (1956) 93.

304. G.C.PIMENTAL and A.L.McCLELLAN, *The Hydrogen Bond, Freeman, San Francisco*, (1960) p.158.

305. G.C.PIMENTAL, *J.Amer.Chem.Soc.*, 79 (1957) 3323.

306. D.P.GRADDON and G.M.MOCKLER, *Aust.J.Chem.*, 20 (1967) 21.

307. C.A.FLEMING and D.A.THORNTON, *J.Mol.Structure*, 17 (1973) 79. and references cited therein.

308. G.C.PERCY and D.A.THORNTON, *J.Inorg.Nucl.Chem.*, 35 (1973) 2719.

309. L.G.HULETT and D.A.THORNTON, *J.Inorg.Nucl.Chem.*, 35 (1973) 2661.

310. C.K.JORGENSEN, *Acta Chem. Scand.*, 16 (1962) 2406.

311. G.KARABATSOS, *J.Org.Chem.*, 25 (1960) 315.

312. A.B.P.LEVER, J.LEWIS and R.S.NYHOLM, *J.Chem.Soc.*, (1962) 5262.

313. B.N.FIGGIS, *Nature*, 182 (1958) 1568.

314. B.N.FIGGIS and R.S.HYHOLM, *J.Chem.Soc.*, (1959) 338.

315. F.A.COTTON, O.D.FAUT and J.T.MAGUE, *Inorg.Chem.*, 3 (1964) 17.

316. R.L.CARLIN and S.L.HOLT, *Inorg.Chem.*, 2 (1963) 849.

317. F.A.COTTON, D.M.L.GOODGAME, M.GOODGAME and A.SACCO, *J.Amer.Chem.Soc.*, 83 (1961) 4157.

318. A.B.P.LEVER, *Inorganic Electronic Spectroscopy, Elsevier, Amsterdam*, (1968).

319. N.S.GILL and R.S.NYHOLM, *J.Chem.Soc.*, (1959) 3997.

320. L.SACCONI, P.NANELLI, N.NARDI and U.CAMPIGLI, *Inorg.Chem.*, 4 (1965) 943.

321. L.SACCONI, I.BERTINI and R.MORASSI, *Inorg.Chem.*, 6 (1967) 1548.

322. L.SACCONI, *Pure Appl.Chem.*, 17 (1968) 95.

323. C.FURLANI, *Coord.Chem.Revs.*, 3 (1968) 141.

324. M.CIAMPOLINI, *Inorg.Chem.*, 5 (1966) 35.

325. J.S.WOOD, *Progr.Inorg.Chem.*, 16 (1972) 227.

326. M.M.STIMSON, *J.Chem.Phys.*, 22 (1954) 1942.

327. M.DAVIES and R.L.JONES, *J.Chem.Soc.*, (1954) 120.

328. K.NAKAMOTO, J.FUJITA, S.TANAKA and M.KOBAYASHI, *J.Amer.Chem. Soc.*, 79 (1957) 4904.

329. A.G.HILL and C.CURRAN, *J.Phys.Chem.*, 64 (1960) 1519.

330. K.NAKAMOTO, Y.MORIMOTO and A.E.MARTELL, *J.Amer.Chem.Soc.*, 83 (1961) 4528.

331. E.SPINNER, *J.Chem.Soc.* *B*, (1967) 874.

332. C.A.McAULIFFE and W.D.PERRY, *J.Chem.Soc.A*, (1969) 634.

333. I.LAULICHT, S.PINCHAS, D.SAMUEL and I.WASSERMAN, *J.Phys.Chem.*, 70 (1966) 2719.

334. B.N.FIGGIS and R.S.NYHOLM, *J.Chem.Soc.*, (1954) 12.

335. R.L.DUTTA and S.P.BANERJEE, *J.Indian Chem.Soc.*, 51 (1974) 497.

336. G.A.BARCLAY and B.F.HOSKINS, *J.Chem.Soc.*, (1965) 1979.

337. W.E.HATFIELD and F.L.BUNGER, *Inorg.Chem.*, 5 (1966) 1161.

338. A.P.GINSBURG, R.C.SHERWOOD and E.KOUBEK, *J.Inorg.Nucl.Chem.*, 29 (1967) 353.

339. B.BLEANEY and K.D.BOWERS, *Proc.Roy.Soc.*, A214 (1952) 451.

340. E.SINN and C.M.HARRIS, *Coord.Chem.Revs.*, 4 (1969) 416.

341. B.BACCAR, R.MATHIS, A.SECCHES, J.BARRANS and F.MATHIS, *J.Mol.Structure*, 7 (1971) 369.

342. K.L.WIERZCHOWSKI and D.SHUGAR, *Spectrochim. Acta*, 21 (1965) 943.

343. A.BRAIBANTI, F.DALLAVALLE, M.A.PELLINGHELLI and E.LEPORATI, *Inorg.Chem.*, 7 (1968) 1430.

344. L.MESTER, A.STEPHEN and J.PARELLO, *Tet. Lett.*, (1968) 4119.

345. P.B.FISCHER, B.L.KAUL and H.ZOLLINGER, *Helv.Chim.Acta*, 51 (1968) 1449.

346. A.FOFFANI, C.PECILE and S.GHERSETTI, *Tet.Lett.*, (1959) No. 11, 16.

347. C.SCHIELE, *Ber.Bunsenges.Physik.Chem.*, 69 (1965) 308.

348. C.SCHIELE and G.ARNOLD, *Tet.Lett.*, (1966) 4103.

349. L.J.BELLAMY, *Advances in Infra Red Group Frequencies, Methuen, London*, (1968), p.230.

60. K.SHOBATAKE and K.NAKAMOTO, *J.Amer.Chem.Soc.*, 92(1970) 3332.

61. C.UDOVICH, J.TAKEMOTO and K.NAKAMOTO, *J.Coord.Chem.*, 1 (1971) 89.

62. K.SHOBATAKE and K.NAKAMOTO, *J.Amer.Chem.Soc.*, 92 (1970) 3339.

63. A.B.P.LEVER and G.W.RAYNER CANHAM, *Canad.J.Chem.*, 50 (1972) 3866.

64. A.B.P.LEVER and E.MANTOVANI, *Canad.J.Chem.*, 51 (1973) 1567.

65. A.B.P.LEVER and B.S.RAMASWAMY, *Canad.J.Chem.*, 51 (1973) 514.

66. B.HUTCHINSON, D.EVERSDYK and S.OLBRICHT, *Spectrochim. Acta*, 30A (1974) 1605.

67. M.A.J.JUNGBAUER and C.CURRAN, *Spectrochim.Acta*, 20 (1965) 641.

68. I.S.AHUJA, D.H.BROWN, R.H.NUTTALL and D.W.A.SHARP, *J.Inorg. Nucl.Chem.*, 27 (1965) 1105.

69. I.S.AHUJA, D.H.BROWN, R.H.NUTTALL and D.W.A.SHARP, *J.Inorg. Nucl.Chem.*, 27 (1965) 1625.

70. J.M.HAIGH, M.A.VAN DAM and D.A.THORNTON, *J.S.Af.Chem.Inst.*, 20 (1967) 113.

71. M.S.BARVINOK, Y.S.VARSHAVSKII and L.K.PUTSEIKO, *Zh.Neorgan. Khim.*, 6 (1961) 1125.

72. N.G.YAROSLAVSKII and L.V.KONOVALOV, *Prikl.Spektrosk., Mater. Soveshch.*, 16th (1965) No. 2, 35.

73. M.S.BARVINOK, I.S.BUKHAREVA and Y.S.VARSHAVSKII, *Zh.Neorgan. Khim.*, 10 (1965) 2293.

74. M.S.BARVINOK, I.S.BUKHAREVA and Y.S.VARSHAVSKII, *Zh.Neorgan. Khim.*, 10 (1965) 1799.

75. N.G.YAROSLAVSKII and L.V.KONOVALOV, *Dokl.Akad.Nauk SSSR*, 162 (1965) 144.

76. M.S.BARVINOK, I.S.BUKHAREVA, L.V.KONOVALOV and N.G.YAROSLAVSKII, *Zh.Neorgan.Khim.*, 12 (1967) 3076.

77. M.S.BARVINOK, I.S.BUKHAREVA, L.V.KONOVALOV and N.G.YAROSLAVSKII, *Probl.Sovrem.Khim.Koord.Soedin., Leningrad Gos.Univ.*, (1968) No.2, 129.

78. L.V.KONOVALOV and N.G.YAROSLAVSKII, *Teor.Eksp.Khim.*, 6 (1970) 258.

79. M.S.BARVINOK, L.V.KONOVALOV, I.S.MASLENNIKOVA and N.G.YAROSLAVSKII, *Zh.Fiz.Khim.*, 44 (1970) 13.

80. T.V.ZHURBA and V.I.DULOVA, *Ukr.Khim.Zh.*, 37 (1971) 952.

81. I.S.MASLENNIKOVA, *Zh.Fiz.Khim.*, 46 (1972) 168.

82. I.S.MASLENNIKOVA, *Zh.Neorg.Khim.*, 17 (1972) 132.

83. R.H.HOLM and F.A.COTTON, *J.Chem.Phys.*, 32 (1960) 1168.

84. A.B.P.LEVER, *Inorg.Chem.*, 4 (1965) 763.

85. P.LUMME and J.PELTONEN, *Soumen Kemi.*, B36 (1963) 38.

86. R.S.NYHOLM, *Rept. to 10th Solvay Council, Brussels* (1956).

87. G.B.BOKII, T.I.MALINOVSKII and A.V.ABLOV, *Kristallografiya*, 1 (1956) 49.

88. A.V.ABLOV, T.I.MALINOVSKII, *Dokl.Akad.Nauk SSSR*, 123 (1958) 677.

89. T.I.MALINOVSKII, *Kristallografiya*, 2 (1957) 734.

90. T.I.MALINOVSKII, *Kristallografiya*, 3 (1958) 364.

91. T.V.ZHURBA and V.I.DULOVA, *Ukr.Khim.Zh.*, 37 (1971) 308.

92. T.V.ZHURBA and V.I.DULOVA, *Zh.Neorg.Khim.*, 16 (1971) 2190.

93. J.D.DUNITZ, *Acta Cryst.*, 10 (1957) 307.

94. I.S.MASLENNIKOVA and V.N.SHEMYAKIN, *Zh.Neorgan.Khim.*, 17 (1972) 132.

95. S.CALIFANO and R.MOCCIA, *Gazz.Chim.Ital.*, 86 (1956) 1014.

96. S.CALIFANO and R.MOCCIA, *Gazz.Chim.Ital.*, 87 (1957) 805.

97. H.RICHTERING, *Z.Phys.Chem.*, 9 (1956) 393.

98. J.C.EVANS, *Spectrochim. Acta*, 16 (1960) 428.

99. M.TSUBOI, *Spectrochim. Acta*, 16 (1960) 505.

100. J.P. FACKLER, *Progr.Inorg.Chem.*, 7 (1966) 361.

101. D.W.BARNUM, *J.Inorg.Nucl.Chem.*, 21 (1961) 221.

102. D.W.BARNUM, *J.Inorg.Nucl.Chem.*, 22 (1961) 183.

103. J.P. FACKLER, F.A.COTTON and D.W.BARNUM. *Inorg.Chem.*, 2 (1963) 97.

104. F.A.COTTON, C.B.HARRIS and J.J.WISE, *Inorg.Chem.*, 6 (1967) 909.

105. F.A.COTTON and J.J.WISE, *Inorg.Chem.*, 6 (1967) 917.

106. V.I.AVDEEV and I.I.ZAKHAROV, *Teor.Expr.Khim.*, 2 (1966) 609.

107. J.P.FACKLER and F.A.COTTON, *Inorg.Chem.*, 2 (1963) 102.

108. A.D.TANEJA and K.P.SRIVASTAVA, *J.Inorg.Nucl.Chem.*, 35 (1973) 1397.

109. G.E.UTZINGER, *Helv.Chim.Acta*, 31 (1952) 1359.

110. R.L.BELFORD, A.E.MARTELL and M. CALVIN, *J.Inorg.Nucl.Chem.*, 2 (1956) 11.

111. L.WOLF and K.WETZEL, *Ber.*, 90 (1957) 1007.

112. L.KNORR, *Ann.*, 236 (1886) 76.

113. H.O.CHAPLIN and L.HUNTER, *J.Chem.Soc.*, (1939) 484.

114. H.J.HARRIES, *J.Inorg.Nucl.Chem.*, 25 (1963) 519.

115. H.J.HARRIES, *J.Inorg.Nucl.Chem.*, 29 (1967) 2484.

116. H.J.HARRIES, S.SAVAGE, G.WRIGHT and N.LOGAN, *J.Inorg.Nucl. Chem.*, 31 (1969) 2477.

117. H.J.HARRIES and G.WRIGHT, *J.Inorg.Nucl.Chem.*, 31 (1969) 3149.

118. H.J.HARRIES, R.K.HUGHES and T.S.SMITH, *J.Inorg.Nucl.Chem.*, 34 (1972) 1609.

119. G.STÖCKELMAN, A.KETTRUP and H.SPECKER, *Z.Anorg.Allg.Chem.*, 372 (1970) 134.

120. K.P.SRIVASTAVA and A.D.TANEJA, *J.Inst.Chem., Calcutta*, 42 (1970) 148.

121. A.D.TANEJA and K.P.SRIVASTAVA, *J.Inorg.Nucl.Chem.*, 33 (1971) 2678.

122. A.KORKUC, S.ZOMMER and T.LIPIEC, *Theory Struct. Complex.Compds., Papers Symp. Wroclaw, Poland* (1962) 551.

123. A.KETTRUP and H.SPECKER, *Fresenius' Z.Anal.Chem.*, 246 (1969) 108.

124. A.D.TANEJA and K.P.SRIVASTAVA, *J.Inst.Chem., Calcutta*, 44 (1972) 28.

125. A.KETTRUP, *Fresenius' Z.Anal.Chem.*, 246 (1969) 183.

126. R.L.DUTTA, A.SYAMAL and S.GHOSH, *J.Indian Chem.Soc.*, 43 (1966) 526.

127. R.L.DUTTA and A.SYAMAL, *J.Indian Chem.Soc.*, 44 (1967) 381.

128. A.SYAMAL and R.L.DUTTA, *J.Indian Chem.Soc.*, 45 (1968) 1.

129. A.SYAMAL, *J.Indian Chem.Soc.*, 45 (1968) 374.

130. A.SYAMAL, *J.Indian Chem.Soc.*, 45 (1968) 347.

131. A.SYAMAL, *J.Prakt.Chem.*, 312 (1970) 954.

132. A.P.BUDKHAR, P.UMAPATHY and D.N.SEN, *Indian J.Chem.*, 9 (1971) 376.

133. A.D.TANEJA, K.P.SRIVASTAVA and N.K.AGARWAL, *J.Inorg.Nucl. Chem.*, 34 (1972) 3573.

134. A.SYAMAL, *J.Indian Chem.Soc.*, 45 (1968) 461.

135. A.SYAMAL and R.L.DUTTA, *Indian J.Chem.*, 6 (1968) 520.

136. D.N.SEN and N.THANKARAJAN, *Indian J.Chem.*, 6 (1968) 746.

137. A.SYAMAL, *J.Indian Chem.Soc.*, 45 (1968) 904.

138. S.K.SHAH, M.R.PATEL and B.N.MANKAD, *Indian J.Chem.*, 8 (1970) 607.

139. A.SYAMAL, *Z.Naturforsch.*, B26 (1971) 320.

140. A.D.TANEJA, *J.Inorg.Nucl.Chem.*, 35 (1973) 3617.

141. D.N.SEN and P.UMAPATHY, *Indian J.Chem.*, 6 (1968) 516.

142. D.N.SEN and N.THANKARAJAN, *Indian J.Chem.*, 6 (1968) 278.

143. K.P.SRIVASTAVA and A.D.TANEJA, *Chem.Age,India*, 21 (1970) 595.

144. A.SYAMAL, *Z.Naturforsch.*, B27 (1972) 867.

145. K.P.SRIVASTAVA and A.D.TANEJA, *Bull., Inst.Chem., Acad.Sinica.*, (1972) No. 19-20, 42.

146. A.D.TANEJA, K.P.SRIVASTAVA and N.K.AGARWAL, *J.Inorg.Nucl. Chem.*, 34 (1972) 2980.

147. V.C.SWETT and E.P.DUDEK, *J.Phys.Chem.*, 72 (1968) 1244.

148. E.P.DUDEK and M.BARBER, *Inorg.Chem.*, 5 (1966) 375, 395.

149. J.N.PATIL and D.N.SEN, *Indian J.Chem.*, 11 (1973) 782.

150. S.K.BHASIN, P.UMAPATHY and D.N.SEN, *J.Indian Chem. Soc.*, 49 (1972) 1113.

151. A.N.GARG, P.N.SHUKLA and P.S.GOEL, *Chem.Phys.Lett.*, 7 (1970) 494.

152. J.DAS and S.BANERJEE, *Z.Anal.Chem.*, 184 (1961) 110.

153. A.K.SARKER and J.DAS, *J.Indian Chem.Soc.*, 48 (1971) 817.

154. K.DATTA and J.DAS, *Indian J.Technol.*, 10 (1972) 76.

155. A.SYAMAL, *J.Inorg.Nucl.Chem.*, 31 (1969) 1869.

156. W.ZANKOWSKA-JASINSKA and I.HOLAK, *Zesz.Nauk Unie. Jagiellon., Pr.Chem.* No. 18 (1973) 125.

157. A.SYAMAL, *J.Prakt.Chem.*, 312 (1970) 954.

158. A.SYAMAL, *Canad.J.Chem.*, 47 (1969) 1693.

159. A.K.SARKER and J.DAS, *Fresenius' Z.Anal.Chem.*, 254 (1971) 364.

160. A.D.TANEJA and K.P.SRIVASTAVA, *J.Inorg.Nucl.Chem.*, 33 (1971) 2694.

161. A.D.TANEJA and K.P.SRIVASTAVA, *J.Chin.Chem.Soc., (Taipei)*, 19 (1972) 173.

162. K.P.SRIVASTAVA and A.D.TANEJA, *Microchem.J.* 17 (1972) 540.

163. A.SYAMAL, D.H.FRICKS, D.C.PANTALEO, P.G.KING and R.C.JOHNSON, *J.Less-common Metals*, 19 (1969) 141.

164. A.SYAMAL, *Z.Anorg.Allg.Chem.*, 373 (1970) 204.

165. A.SYAMAL, *J.Inorg.Nucl.Chem.*, 31 (1969) 1850.

166. A.K.SARKER and J.DAS, *Anal.Chem.*, 39 (1967) 1608.

167. A.SYAMAL, *Inorg. Nucl. Chem.Lett.*, 4 (1968) 543.

168. N.K.CHAUDHURI and J.DAS. *Fresenius' Z.Anal.Chem.*, 255 (1971) 34.

169. A.SYAMAL, *J.Indian Chem.Soc.*, 45 (1968) 755.

170. A.K.SARKER and J.DAS, *Anal.Lett.*, 1 (1968) 323.

171. S.K.MANDAL and J.DAS, *J.Indian Chem.Soc.*, 50 (1973) 424.

172. C.ETTLING, *Ann.*, 35 (1840) 241.

173. H.SCHIFF, *Ann.*, 150 (1869) 193.

174. R.H.HOLM, G.W.EVERETT and A.CHAKRAVORTY, *Progr.Inorg.Chem.*, 7 (1966) 83.

175. L.SACCONI, *Coord.Chem.Revs.*, 1 (1966) 126.

176. S.YAMADA, *Coord.Chem.Revs.*, 1 (1966) 415.

177. E.K.BAREFIELD, D.H.BUSCH and S.M.NELSON, *Quart.Revs.*, 22 (1968) 457.

178. R.H.HOLM and M.J.O'CONNOR, *Progr.Inorg.Chem.*, 14 (1971) 329.

179. P.RAY and A.K.MUKHERJEE, *J.Indian Chem.Soc.*, 27 (1950) 707.

180. A.K.MUKHERJEE and P.RAY, *J.Indian Chem.Soc.*, 32 (1955) 505.

181. Y.MUTO, *Nippon Kagaku Zasshi*, 76 (1955) 1407.

182. M.KISHITA, Y.MUTO and M.KUBO, *Naturwiss.*, 44 (1957) 612.

183. M.KISHITA, Y.MUTO and M.KUBO, *Aust.J.Chem.*, 11 (1958) 309.

184. M.KUBO, Y.KURODA, M.KISHITA and Y.MUTO, *Aust.J.Chem.*, 16 (1958) 7.

185. H.S.VERTER and A.E.FROST, *J.Amer.Chem.Soc.*, 82 (1960) 85.

186. A.K.MAJUMDAR and B.C.BHATTACHARYYA, *J.Inorg.Nucl.Chem.*, 28 (1966) 1215.

187. A.K.MAJUMDAR and B.C.BHATTACHARYYA, *J.Inorg.Nucl.Chem.*, 30 (1966) 1116.

188. M.E.SOIFER, A.S.KUDRYAVTSEV and I.A.SAVICH, *Vestn.Mosk.Univ. Khim.*, 24 (1969) 117.

189. M.E.SOIFER, A.S.KUDRYAVTSEV and I.A.SAVICH, *Pharm.Chem.J.*, 2 (1968) 21.

190. M.E.SOIFER and I.A.SAVICH, *Pharm.Chem.J.*, 2 (1968) 423.

191. R.K.MEHTA, S.P.RAO and R.C.KAPOOR, *Vijnana Parishad Anusandhan Patrika*, 11 (1968) 171.

192. R.K.MEHTA, S.P.RAO and R.C.KAPOOR, *Indian J.Chem.*, 7 (1969) 933.

193. K.D.BUTLER, K.S.MURRAY and B.O.WEST, *Aust.J.Chem.*, 24 (1971) 2249.

194. R.L.DUTTA, D.DE and A.SYAMAL, *J.Indian Chem.Soc.*, 44 (1967) 353.

195. R.L.DUTTA and D.DE, *J.Indian Chem.Soc.*, 46 (1969) 62.

196. R.L.DUTTA and G.P.SEN GUPTA, *J.Indian Chem.Soc.*, 44 (1967) 738.

197. R.L.DUTTA and G.P.SEN GUPTA, *J.Indian Chem.Soc.*, 49 (1972) 919.

198. R.K.MEHTA, V.C.SINGHI, R.K.GUPTA and S.L.PANIA, *J.Indian Chem.Soc.*, 50 (1973) 721.

199. R.K.MEHTA and R.K.GUPTA, *Canad.J.Chem.*, 50 (1972) 1609.

200. M.KATO, H.B.JONASSEN and J.C.FANNING, *Chem.Revs.*, 64 (1964) 99.

201. NG.PH.BUU-HOÏ, NG.D.XUONG, NG.H.NAM, F.BINON and R.ROYER, *J.Chem.Soc.*, (1953) 1358.

202. J.C.CRAIG, D.WILLIS, S.D.RUBBO and J.EDGAR, *Nature*, 176 (1955) 34.

203. E.SORKIN, W.ROTH and H.ERLENMEYER, *Helv.Chim.Acta*, 35 (1952) 1736.

Band Assignments in the Infrared Spectra of p-Toluidine and Its Complexes with Metal(II) Chlorides

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INFRARED SPECTRA OF METAL(II) 1,3,5-TRIARYLFORMAZAN COMPLEXES

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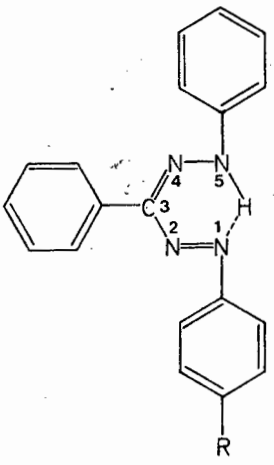
ABSTRACT

1,3,5-Triphenylformazan and its Co(II), Ni(II) and Cu(II) complexes have been labelled with ^{15}N at one of the nitrogen donors. Shifts in infrared bands induced by ^{15}N-labelling, metal ion substitution and ligand substitution are used to assign intraligand and metal-ligand vibrations. Structural implications of the observed shifts are discussed.

INTRODUCTION

1,3,5-Triarylformazans and their metal(II) chelates have elicited structural and spectroscopic interest.[1-8] In an



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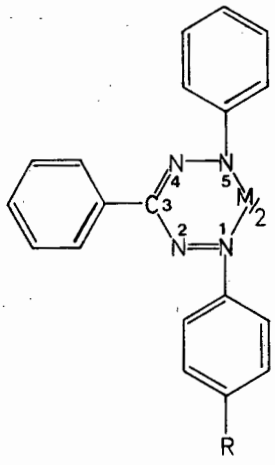

(II)

plex was prepared by precipitation at 25°C from solutions of the ligand and copper(II) acetate in methanol. The ^{15}N-labelled compounds were prepared from ^{15}N-aniline of 95 atom per cent purity supplied by Prochem Ltd. Purity of all compounds was established by microanalysis. Infrared spectra (on Nujol mulls between caesium iodide plates) were determined on a Beckman IR-12 spectrophotometer. At least five determinations were made of each ^{15}N-sensitive band. Magnetic moments, determined by the Gouy method, yielded the following values (μ_{eff}) for the complexes of triphenylformazan: Co(II) (independent samples): 1.98, 2.24 B.M. (reported[4] 1.93 B.M.); Ni(II): diamagnetic; Cu(II): 1.77 B.M.

RESULTS AND DISCUSSION

Table 1 lists the assigned bands in the spectrum of triphenylformazan with shifts induced by ^{15}N-labelling of N^1 and N^2. The results indicate the need for revision of some earlier assignments.

these uncoupled vibrations. Nevertheless, any band comprising a predominant contribution from νC=N should shift significantly on labelling N^2 but not N^1 while bands comprising a major contribution from νN=N should shift on labelling both N^1 and N^2. The bands of highest frequency which satisfy these criteria are at 1517 cm^{-1} (predominantly νC=N) and 1237 cm^{-1} (predominantly νN=N). Labelling of the N^1 atom in the present work enables distinction between the vibrations of the C-N species within the chelate ring and the exocyclic C-N moiety, designated νC-N(exo). The latter vibration should be sensitive to labelling of N^1 but not N^2; hence the 1317 and 1187 cm^{-1} bands are assigned to this mode. Assignments of other vibrations are based on similar arguments in conjunction with empirical assignments.

The Co(II), Ni(II) and Cu(II) complexes of triphenylformazan do not exhibit a precise band-for-band correspondence in their infrared spectra (Fig. 1). This feature suggests that the complexes are not structurally identical although the differences in the band patterns are not sufficiently large as to imply any gross differences in symmetry. Below 700 cm^{-1}, the bands exhibiting maximum sensitivity to labelling of the N^1 atom occur within the range 550-620 cm^{-1} and are therefore assigned as the principal νM-N bands. Their frequencies are metal ion dependent in the order Co>Ni<Cu.

It has been demonstrated[9] that the νM-N values of a pair of isomorphous square planar complexes (M=Ni,Cu) are in the sequence Ni>Cu. This sequence reflects the stability order expected on theoretical grounds, since the antibonding

planar Ni(II) complex, the νM-N sequence Co>Ni>Cu would be expected. The observed order Co>Ni<Cu implies either that the chelate ring is more severely buckled in the Ni(II) than in the Cu(II) complex (buckling would lead to loss of ligand π-function) or that the phenyl groups in the Cu(II) complex are accommodated by some alternative structural feature such as distortion towards tetrahedral symmetry. The latter explanation seems less likely since we and others[3] have failed to synthesize Zn(II) formazan complexes in which tetrahedral coordination would probably occur. These structural problems remain to be resolved by crystallographic studies on the Co(II) and Cu(II) complexes.

It has frequently been found that νM-L bands in metal chelates are shifted by substitution in the ligand (R-sensitive bands). Good correlations have been observed[9,11-13] between the electronic effects of the substituents and νM-L. In the formazan complexes, νM-N is likely to be affected most by substituents in the aryl ring bound to N^1 (or N^5). We therefore synthesized a range of Ni(II) complexes with various substituents (R in formula II) in this ring. Their spectra reveal that the band assigned to νNi-N on the basis of its ^{15}N- and M-sensitivities is also shifted by ligand substitution (Table 2). The R-sensitivity of this band correlates with the Hammett σ- values of the substituents. As would be expected, electron-withdrawing substituents decrease νM-N and electron-releasing substituents increase νM-N (relative to R = H).

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REFERENCES

1. L. Hunter and C.B. Roberts, *J. Chem. Soc.* 820, 823 (1941).

2. R.J.W. Le Fèvre, J.B. Sousa and R.L. Werner, *Austral. J. Chem.* 9, 151 (1956).

3. H. Irving, J.B. Gill and W.R. Cross, *J. Chem. Soc.* 2087 (1960).

4. M.I. Ermakova, E.I. Krylov and I. Ya. Postovskii, *Zhur. Obschei Khim.* 30, 849 (1960).

5. D. Dale, *J. Chem. Soc.* (A) 278 (1967).

6. G. Arnold and C. Schiele, *Spectrochim. Acta* 25A, 685, 697 (1969).

7. W. Otting and F.A. Neugebauer, *Chem. Ber.* 102, 2520 (1969).

8. R. Price, *J. Chem. Soc.* (A) 3379 (1971).

9. G.C. Percy and D.A. Thornton, *J. Inorg. Nucl. Chem.* 34, 3357 (1972).

10. K.L. Wierzchowski and D. Shugar, *Spectrochim. Acta* 21, 943 (1965).

11. G.S. Shephard and D.A. Thornton, *J. Molec. Structure* 16, 321 (1973).

12. C.A. Fleming and D.A. Thornton, *J. Molec. Structure* 17, 79 (1973).

13. G.C. Percy and D.A. Thornton, *J. Inorg. Nucl. Chem.* 35, 2319, 2719 (1973).

14. D.H. McDaniel and H.C. Brown, *J. Org. Chem.* 23, 420 (1958).

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BENZOYLACETANILIDE COMPLEXES OF COPPER(II)

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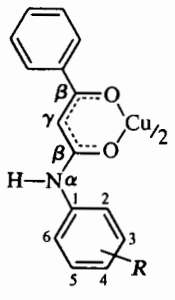
Abstract—The synthesis of twenty copper(II) complexes of benzoylacetanilides variously substituted in the anilide ring, is described. Their general formula is $[CuL_2]$ (L = 3- or 4-substituted benzoylacetanilide anion. Contrary to an earlier report, the complexes have normal magnetic moments ($\mu_{eff} \sim 1{\cdot}8$ B.M. at 295 K). The green complexes with substituents in the 3-position of the anilide ring undergo solvent adduction by methanol to yield brown complexes of formula $[CuL_2(\text{methanol})_2]$. Copper–oxygen stretching frequencies are assigned to infrared bands which shift in the sequence of the electronic effects of the substituents. A band near 30 kK (1 kK = 10^3 cm^{-1}) in the electronic spectra is assigned to the ligand $\pi_3 \rightarrow \pi_4^*$ transition. The shift towards lower energies induced in this band by substituents with electron withdrawing resonance effects indicates that metal–ligand π-bonding is not significant in copper(II) benzoylacetanilide complexes. Intense absorption near 40 kK is assigned to a $\sigma_L \rightarrow 3d_{xy}$ transition. Weak $d \rightarrow d$ bands occur near 15 kK.

INTRODUCTION

BENZOYLACETANILIDE is the parent member of a novel clase of β-diketones in which a phenyl and an arylamino group replace the two methyl substituents of acetylacetone. The copper(II) complex, in which coordination is considered to take place through the oxygen atoms, has recently [1] elicited interest. This paper reports the synthesis, magnetic and spectroscopic properties of a wide range of copper(II) complexes of benzoylacetanilides in which the anilide ring contains a variety of 3- and 4-substituents (Formula I).



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EXPERIMENTAL

Ligands were synthesized by the method described [2] for benzoylacetanilide employing the appropriately substituted amine. The complexes $[CuL_2]$ were prepared by mixing solutions of copper(II) acetate and the ligand in ethanol. Difficulty was experienced in obtaining analytically pure complexes by Syamal's procedure [1] employing copper(II) chloride and ammonia. Three of the complexes (I; R = H, 3-Br and 4-OCH_3) were prepared by both methods, the pairs of complexes have identical i.r. spectra and magnetic moments. The methanol adducts of the 3-substituted benzoylacetanilides were obtained by triturating the complexes $[CuL_2]$ with methanol. The adducts were filtered off, washed with methanol and dried in air at atmospheric pressure. The following magnetic moments were recorded (substituent followed by μ_{eff} in B.M. at 295 K in parentheses): H(1·82); 4-OCH_3 (1·83); 4-NO_2 (1·83); 3-Br (1·77); 3-Cl (1·79); 3-Cl methanol adduct (1·74).

I.R. spectra were determined on a Beckman IR-12 spectrophotometer employing Nujol mulls between caesium iodide plates. Solution and reflectance electronic spectra were determined on a Beckman DK-2A spectrophotometer. Spectra of the sodium salts were determined by dissolving the ligands in methanol containing sodium methoxide slightly in excess of stoichiometric quantity. Magnetic moments were determined on a Newport–Stanton magnetic balance.

RESULTS AND DISCUSSION

Syamal [1] described the Cu(II) complex of benzoylacetanilide (I, R = H) as a green, crystalline compound of formula $[CuL_2]$ with a subnormal magnetic moment (μ_{eff} = 1·40 B.M.) considered indicative of Cu–Cu interaction. We find this complex and those containing a variety of anilide substituents to have normal room temperature moments within the range 1·74–1·83 B.M. The

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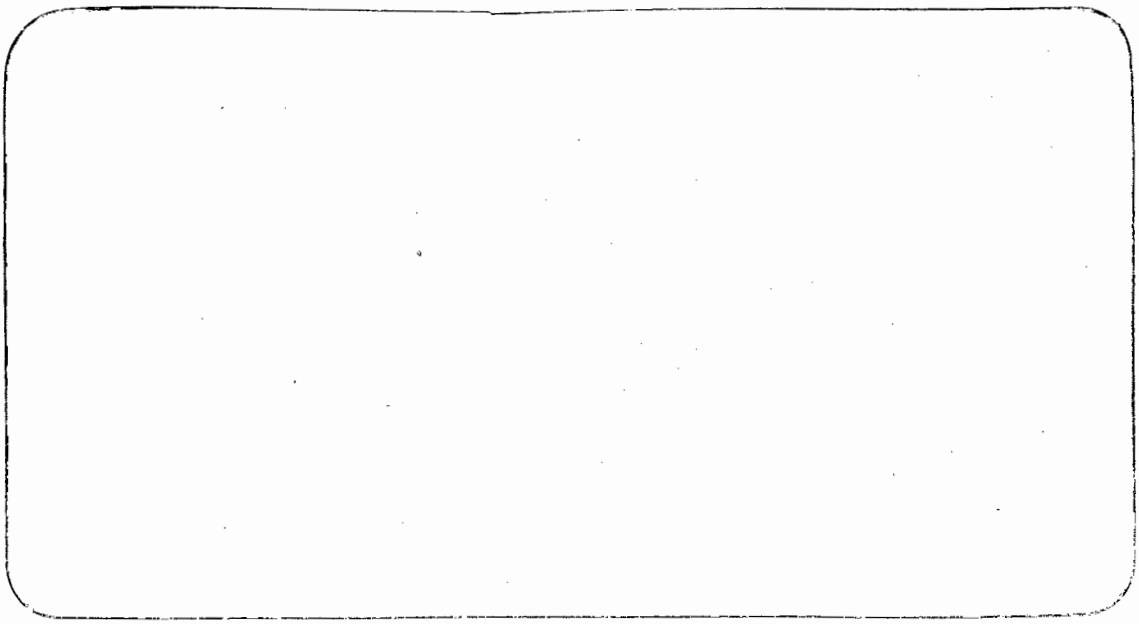

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ELECTRONIC SPECTRA OF COPPER(II) β-KETOENOLATES: INTRALIGAND AND CHARGE TRANSFER TRANSITIONS

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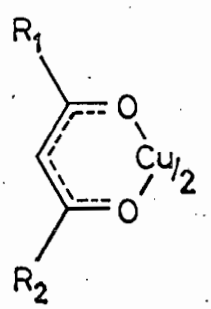
(Received January 1975)

ABSTRACT

The electronic spectra (in methanol) of the sodium salts and copper(II) complexes of thirteen β-diketones are reported within the energy range 25 to 48 kK. Spectra of the sodium salts of ligands with alkyl substituents exhibit one band which is assigned to the $\pi_3 \rightarrow \pi_4$ intraligand transition. Where aryl substituents are present, an additional benzenoid band is observed. The spectra of the copper complexes exhibit two bands whether aryl substituents are present or not. The band of lower energy is assigned to the $\pi_3 \rightarrow \pi_4$ transition and the band of higher energy to the $\sigma_L \rightarrow 3d_{xy}$ charge transfer transition. Intensity relationships suggest that, where aryl substituents are present, the benzenoid band is superimposed on the charge transfer band. The observed transition energies exhibit a good level of agreement with those predicted by Hückel MO calculations. Comparison of the $\pi_3 \rightarrow \pi_4$ transition energies of the copper complexes with those available for



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the β-ketoenolates of other metal ions supports indications from ESR spectra that there is very little π-orbital overlap in the copper-oxygen bonds.

INTRODUCTION

In a previous paper [1] the assignments of intraligand $\pi_3 \rightarrow \pi_4$ and charge transfer bands in the electronic spectra of octahedral metal(III) β-ketoenolates were discussed. This paper deals with the corresponding assignments in the spectra of thirteen copper(II) β-ketoenolates of general formula (I).

The spectra of a number of complexes of general formula (I) have been reported [2]. While it is generally agreed that the absorption within the range 27 to 35 kK originates in the $\pi_3 \rightarrow \pi_4$ transition, there is some lack of agreement [3-5] on the assignment of the band near 40 kK. The results [4-7] of a semi-empirical Hückel MO treatment of a generalised copper(II) β-ketoenolate have been applied to the interpretation of the spectra of certain complexes of formula (I) in which R_1 and R_2 are alkyl substituents. Allowing for a small degree of $d\pi$-$p\pi$ overlap in the copper-oxygen bonds, the calculations predict symmetry-allowed transitions of moderate to high oscillator strength near 33 and 36 kK ($\pi_3 \rightarrow \pi_4$), 48 and 51 kK ($\pi_3 \rightarrow \pi_5$) and 42 kK ($\sigma_L \rightarrow 3d_{xy}$). The small separation between the energies of the components of the $\pi \rightarrow \pi^*$ transitions implies that they are likely to be observed as single bands in solution

spectra. Since the principal aim of the present study was to establish the origin of the 40 kK band by a comparison of both the energies and intensities of bands in the spectra of the sodium salts with those of the copper complexes of the same β-ketoenolate ligands, we had perforce to use a common solvent (methanol) which precluded measurements above 48 kK. Within the range of measurement (25 to 48 kK) the observed spectra of the copper complexes exhibit two bands. On the strength of the MO calculations [5-7] the band of lower energy has been assigned to the $\pi_3 \rightarrow \pi_4$ transition and the band at higher energy (also originally [4] assigned to the $\pi_3 \rightarrow \pi_4$ transition) has been re-assigned to the charge transfer ($\sigma_L \rightarrow 3d_{xy}$)transition. Nevertheless, the earlier assignment persists in some recent work [3]. Recently [9], in discussing the properties of copper(II) benzoylacetanilide complexes (I; $R_1 = C_6H_5$, $R_2 = NH\text{-}C_6H_4\text{-}R$) we favoured the charge transfer assignment but the argument was clouded by the presence of aryl rings which are themselves expected to yield benzenoid bands near 40 kK. In the present work, the inclusion of ligands with and without aryl substituents, enables the origin of the 40 kK band to be established more conclusively.

EXPERIMENTAL

Solutions of the sodium salts were obtained by addition of a fifty-fold molar excess of sodium methoxide to methanol solutions of the ligands. Spectra of the copper complexes

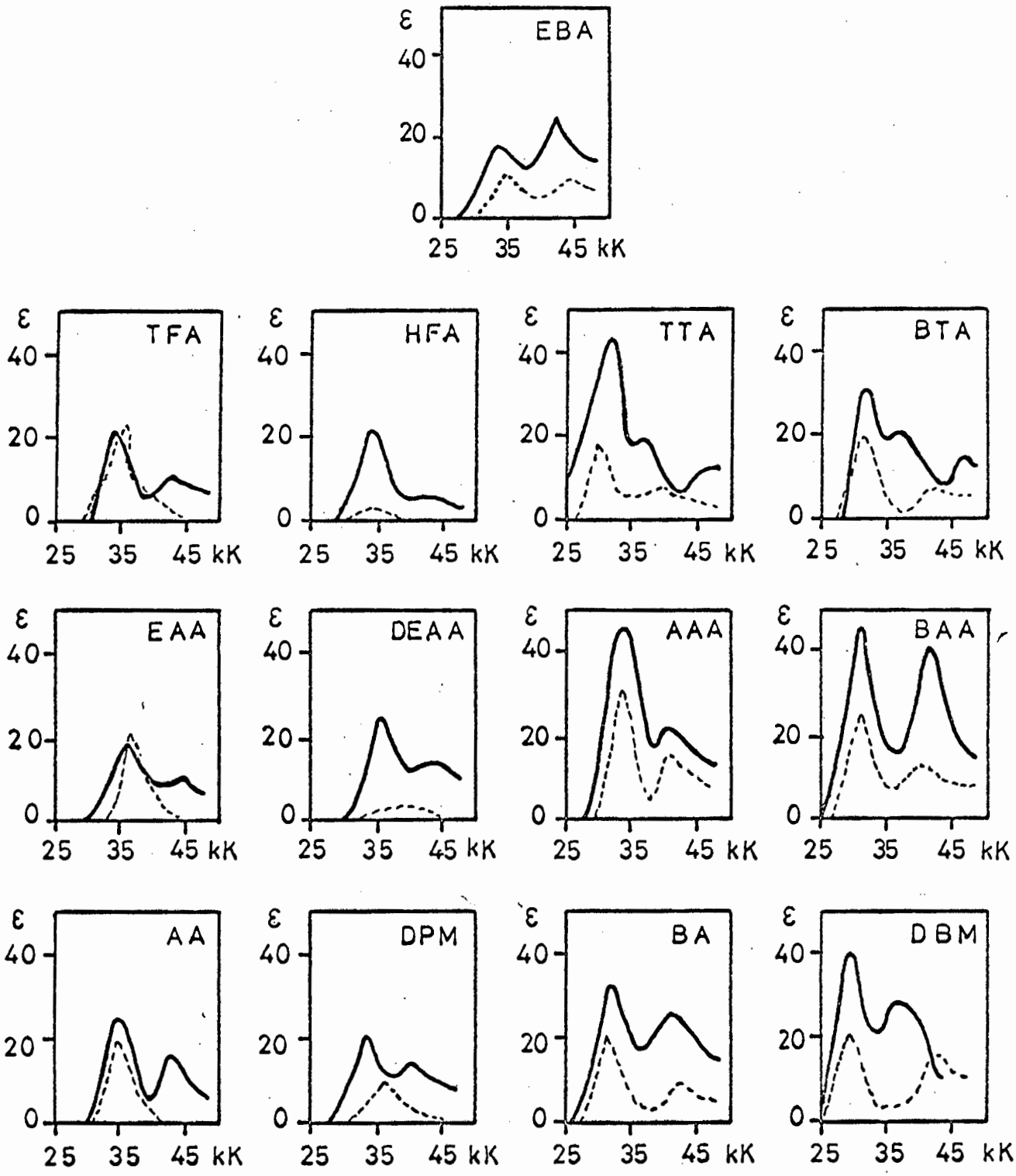

Figure 1. Electronic spectra of copper complexes(_____) and sodium salts(-------) of β-ketoenolates.

were determined in methanol solution except for the insoluble [Cu(DBM)$_2$] which was determined in chloroform solution. Spectra were determined on a Beckman DK-2A spectrophotometer.

RESULTS AND DISCUSSION

The spectra of the sodium salts and copper complexes are depicted in Fig. 1; the transition energies and molar absorptivities are listed in Table 1.

Ligands with alkyl substituents

The spectra of the sodium salts of these ligands exhibit a single intense band between 33 and 39 kK. The band is assigned to the $\pi_3 \rightarrow \pi_4$ transition in agreement with both Hückel and SCF calculations [2].

The spectra of the copper complexes of these ligands exhibit two intense bands near 35 and 42 kK. The MO calculations [5-7] show that the two symmetry-allowed components ($b_{2g} \rightarrow a_u$ and $b_{1u} \rightarrow b_{3g}$) of the $\pi_3 \rightarrow \pi_4$ transition which result from copper-oxygen π-bonding both move towards higher energy with increased $p\pi$-$d\pi$ overlap and that the very small separation energy between the components is maintained over all reasonable strengths of the π-bond. It is therefore unlikely that the two bands in the spectra of the copper complexes both originate in the $\pi_3 \rightarrow \pi_4$ transition. Furthermore, a $\pi_3 \rightarrow \pi_4$ transition energy as high as 42 kK would necessitate the assumption of considerable π-orbital

overlap in contradiction of ESR evidence [10] which indicates a very low level of π-bonding in copper β-ketoenolates. If a small extent of π-overlap is assumed, the energy of the 35 kK band in the spectra of the copper complexes fits the calculated $\pi_3 \rightarrow \pi_4$ transition energy very well; the 35 kK band is accordingly assigned to both components of this transition.

Having established that the band near 42 kK is unlikely to be a component of the $\pi_3 \rightarrow \pi_4$ transition, we will consider two other reasonable assignments for this band. Assignment to the $\pi_3 \rightarrow \pi_5$ transition is rejected for two reasons. Firstly, the observed energy is well below that determined for the $\pi_3 \rightarrow \pi_5$ transition by the MO calculations [5-7] which place the two symmetry-allowed components of this transition near 48 and 51 kK in the absence of copper-oxygen π-bonding and at even higher energies if some π-overlap is assumed (under favourable circumstances, i.e. where the complexes are soluble in cyclohexane, a strong band near 50 kK is observed [5]; this band is more logically assigned to the $\pi_3 \rightarrow \pi_5$ transition). Secondly, the observation that the $\pi_3 \rightarrow \pi_4$ transition energies are very similar for both the sodium salt and copper complex of each ligand, suggests that this should hold also for the $\pi_3 \rightarrow \pi_5$ transition energies whereas no band is observed in the 42 kK region of the sodium salt spectra. The remaining reasonable assignment for the 42 kK band is to the charge transfer

TABLE 1

TRANSITION ENERGIES, MOLAR ABSORPTIVITIES AND BAND ASSIGNMENTS IN ELECTRONIC SPECTRA OF Na(I) AND Cu(II) β-KETOENOLATES[a]

R_1	R_2	*Ligand abbreviation*[b]	*Sodium salt*		*Copper complex*	
			$\pi_3 \rightarrow \pi_4$ *benzenoid*		$\pi_3 \rightarrow \pi_4$	$\sigma_L \rightarrow 3d_{xy}$[c]
			$kK(\varepsilon)$	$kK(\varepsilon)$	$kK(\varepsilon)$	$kK(\varepsilon)$
Alkyl-substituted β-ketoenolates						
CF_3	CF_3	HFA	33.1 (2150)		32.8 (21070)	42.2 (6360)
CF_3	CH_3	TFA	34.1 (19050)		33.9 (20430)	42.6 (11050)
$C(CH_3)_3$	$C(CH_3)_3$	DPM	36.0 (8630)		33.7 (21350)	39.8 (14770)
CH_3	CH_3	AA	34.1 (20280)		34.3 (25850)	41.7 (14510)
CH_3	$N(C_2H_5)_2$	DEAA	38.9 (2110)		36.1 (23160)	42.6 (13390)
CH_3	OC_2H_5	EAA	36.9 (20680)		36.4 (16530)	44.4 (8520)
Aryl-substituted β-ketoenolates						
C_6H_5	C_6H_5	DBM	28.8 (23100)	41.8 (14580)	28.7 (40550)	37.6 (29780)
C_6H_5	CH_3	BA	30.9 (21180)	42.0 (10420)	31.3 (33800)	39.1 (26960)
CF_3	thenoyl	TTA[d]	29.9 (17920)	38.8 (7640)	32.0 (42920)	36.0 (17270)
C_6H_5	NHC_6H_5	BAA	30.3 (24540)	39.8 (13930)	30.8 (46490)	40.8 (40590)
CH_3	NHC_6H_5	AAA	33.6 (29530)	41.3 (15620)	34.1 (47400)	40.8 (20320)
CF_3	C_6H_5	BTA[e]	31.1 (20420)	41.8 (9570)	30.9 (32120)	36.9 (24110)
C_6H_5	OC_2H_5	EBA	33.0 (11500)	43.7 (10280)	33.0 (18560)	41.5 (24800)

[a] In methanol, except for $[Cu(DBM)_2]$ (in chloroform).

[b] Abbreviations: HFA = hexafluoroacetylacetonate, TFA = trifluoroacetylacetonate, DPM = dipivaloylmethanate, AA = acetylacetonate, DEAA = N,N-diethylacetoacetamide, EAA = ethyl acetoacetate, DBM = dibenzoylmethanate, BA = benzoylacetonate, TTA = 2-thenoyltrifluoroacetonate, BAA = benzoylacetanilide, AAA = acetoacetanilide, BTA = benzoyltrifluoroacetonate, EBA = ethyl benzoylacetate.

[c] Superimposed on benzenoid band in aryl-substituted β-ketoenolates.

[d] Additional band near limit of measurement (~48 kK)

[e] Additional band at 46.3 kK (ε = 18570) assigned to $\pi_3 \rightarrow \pi_5$ transition.

($\sigma_L \rightarrow 3d_{xy}$) transition which the MO calculations [5-7] place very near 42 kK. In the present work, absence of a corresponding band in the spectra of the sodium salts is the major evidence favouring this assignment.

Ligands with aryl or heterocyclic substituents

Whereas the spectra of the sodium salts of the alkyl-substituted β-ketoenolates exhibit one band near 35 kK, the sodium salts of ligands with aryl substituents yield two intense bands near 30 and 40 kK. This feature suggests that the additional band originates in a transition associated with the aryl ring. Monosubstituted benzenes characteristically yield [11] benzenoid bands within the range 35 to 45 kK. These bands are usually of lower intensity than $\pi \rightarrow \pi^*$ bands although their intensities are increased by resonance conjugation with the substituents. In the spectra of the sodium β-ketoenolates with aryl substituents, the molar absorptivities of the 30 and 40 kK bands are generally in the approximate ratio 2:1. Both the energy and relative intensity of the 40 kK band suggest that it be assigned to a benzenoid band which acquires some gain in intensity through conjugation with the β-ketoenolate ion.

The spectra of the copper complexes of the aryl-substituted ligands also exhibit two bands near 30 and 40 kK. The 30 kK band is assigned to the $\pi_3 \rightarrow \pi_4$ transition for similar reasons to those advanced for the 35 kK band.

in the spectra of the alkyl-substituted copper complexes. That the transition energy is lower and the intensity higher in the aryl series is consistent with the expected effects of the increased electron path imposed by conjugation of the aryl ring with the chelate ring [4].

So far as the origin of the 40 kK band in the spectra of the copper complexes is concerned, we note that the ratio between the molar absorptivities of the 40 kK and $\pi_3 \rightarrow \pi_4$ bands is generally considerably greater for the complexes with aryl substituents than for those with no aryl substituents. This feature suggests that, in the aryl series, the 40 kK band acquires additional intensity from a chromophore which is unique to this series, i.e. the phenyl ring. We therefore consider that, in the copper complexes of aryl-substituted ligands, the 40 kK band comprises the combined intensities of the benzenoid and $\sigma_L \rightarrow 3d_{xy}$ transitions.

Extent of π-interaction in copper(II) β-ketoenolates

Most of the available evidence from ESR [10] and electronic spectra [4,5,9] suggests that the extent of π-overlap in the copper-oxygen bonds of copper(II) tris-β-ketoenolates is small and certainly significantly less than that which exists [1] in most octahedral (β-ketoenolates) of metal(III) ions of the first transition series. In the present work, the observation that the $\pi_3 \rightarrow \pi_4$ transition energies of the sodium salts and copper complexes of a particular ligand are of similar

magnitude also indicates a low level of π-bonding. The available data [1,8,12] on $\pi_3 \rightarrow \pi_4$ energies for the complexes of eight metal ions with five β-ketoenolate ligands (Table 2) places the Cu(II) ion near Al(III) (in the complexes of which metal-ligand π-bonding is electronically prevented) and VO(II) (where structural considerations minimise V→O π-bonding). A noteworthy feature of the data in Table 2 is the consistency with which the $\pi_3 \rightarrow \pi_4$ transition energies follow a similar metal ion order for each ligand and a similar ligand order for each metal ion. This observation, of itself, supports the assignment of these bands to a transition of common origin.

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REFERENCES

1. C.A. Fleming and D.A. Thornton, *J.Mol.Struct.*, 25 (1974) 271
2. J.P. Fackler, *Progr.Inorg.Chem.*, 7 (1966) 361.
3. A.D. Taneja and K.P. Srivastava, *J.Inorg.Nucl.Chem.*, 35 (1973) 1397.
4. D.W. Barnum, *J.Inorg.Nucl.Chem.*, 21 (1961) 221; 22 (1961) 183.
5. J.P. Fackler, F.A. Cotton and D.W. Barnum, *Inorg.Chem.*, 2 (1963) 97.

6. F.A. Cotton, C.B. Harris and J.J. Wise, *Inorg.Chem.*, 6 (1967) 909.

7. F.A. Cotton and J.J. Wise, *Inorg.Chem.*, 6 (1967) 917.

8. D. Ogden and J. Selbin, *J.Inorg.Nucl.Chem.*, 30 (1968) 1227.

9. P.R. Johnson and D.A. Thornton, *J.Inorg.Nucl.Chem.*, (1974).

10. A.H. Maki and B.R. McGarvey, *J.Chem.Phys.*, 29 (1958) 31.

11. E.S. Stern and C.J. Timmons, *Electronic Absorption Spectroscopy in Organic Chemistry*, Second edition, Arnold, London, 1970, p. 113.

12. R.D. Hancock and D.A. Thornton, *Theor.Chim.Acta*, 18 (1970) 67.

TABLE 2

$\pi_3 \rightarrow \pi_4$ TRANSITION ENERGIES (kK) OF METAL β-KETOENOLATES

Metal ion	*Ligand→*	*DBM*	*BA*	*TFA*	*DPM*	*AA*	*Ref.*
VO(II)[a]		27.4	30.3	32.7	33.1	32.6	[8]
Cu(II)[b]		28.7	31.3	33.9	33.7	34.3	this work
Na(I)[b]		28.8	30.9	34.1	36.0	34.1	this work
Al(III)[c]		28.6	31.3	34.3	34.0	34.8	[1,12]
Mn(III)[c]		29.1	32.4	34.2	36.5	36.8	[1,12]
Fe(III)[c]		30.0	33.2	36.5	36.2	36.8	[1,12]
Cr(III)[c]		31.2	34.2	35.8	-	37.0	[1,12]
Co(III)[c]		33.6	36.1	38.3	-	39.1	[1,12]

[a] In acetonitrile
[b] In methanol except $[Cu(DBM)_2]$ (in chloroform)
[c] In chloroform